Studies of the Infrared Spectra
of Unsymmetrical Molecules

Thesis

by

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The Band Envelopes of Unsymmetrical Rotator Molecules.

I. Calculation of the Theoretical Envelopes *

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Since the majority of molecules of chemical interest are too heavy to permit resolution of the rotational structure of the infra-red bands, it is of interest to find what information can be derived from a study of the band envelopes. Considerations of the type which Gerhard and Dennison have made for symmetrical molecules have been extended to the unsymmetrical rotator. By the use of an approximation method the envelopes of the three elementary types of band have been calculated for nine different sets of molecular parameters.

INTRODUCTION

THE number of molecules with moments of inertia small enough to permit the resolution and analysis of the rotational structure of the infra-red bands appears to be rather limited. In the majority of cases of interest to the chemist it is an idealization to speak of the bands as consisting of lines, since the spacing of the theoretical lines is less than their breadth must be under the conditions of experiment. Gerhard and Dennison[1] have considered the unresolved bands of symmetrical rotators and have shown that useful information can be obtained from the separations and relative intensities of the maxima. They have calculated a number of band envelopes which we have found very useful in qualitative comparisons. However, the majority of molecules are unsymmetrical and their calculations are inapplicable since with even moderate asymmetry the appearance of the bands is materially modified, especially near their centers.

We have recently observed the spectra of a number of moderately heavy unsymmetrical molecules and have found that the bands may vary considerably in appearance and frequently exhibit distinctive features. For example: In some cases there is only one broad maximum, in others there may be as many as five peaks of unequal intensity. The significance of these features has not always been immediately obvious but their variability suggests that useful information may be obtained from the shapes of the band envelopes alone. To make this possible the theoretical envelopes for various types of molecules must, of course, be known.

The discussions of the unsymmetrical rotator bands which have been given in the literature are quite inadequate for our purposes. Both Dennison[2] and Nielsen[3] have presented diagrams giving the positions and intensities of a few lines as functions of asymmetry, but these plots can give no idea of the intensity distribution in a band since only lines of very low J value are included. Aside from this fact they are restricted

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* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 653.

[1] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).

[2] D. M. Dennison, Rev. Mod. Phys. **3**, 2 (1931).

[3] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).

to planar molecules. The elaboration of such diagrams to the point where they would be of general use is not practical owing to the amount of labor involved in calculating every line of appreciable intensity. Since we are not interested at all in individual lines it seems more sensible to follow a procedure similar to that used by Gerhard and Dennison for the symmetrical molecule. Even this is difficult in the unsymmetrical rotator case, but we have devised a method for calculating the intensity distribution in a band which can be carried out with a reasonable amount of labor. The method involves a number of approximations but the errors should not be excessive and the results are indeed justified by satisfactory agreement between calculated and observed band envelopes.

In the unsymmetrical rotator case one finds a number of complications which are not present in the symmetrical molecule. Two of these concern us at this point. In the first place it is comparatively seldom that the bands are of any simple type. If symmetry elements are entirely lacking the electric moment or change of moment may have components along all three principal axes of inertia. It is convenient, however, to consider any band as being built up of the three elementary types of structure which would be expected if the electric moment were parallel to the minor, intermediate or major axis in turn. We shall follow Nielsen in designating these structures by the letters A, B and C, respectively. There has been no consistent usage followed in the literature but it is convenient to adopt the convention that the three principal moments of inertia shall be designated by the same three symbols and always in the order $A<B<C$. The reciprocals, designated by small letters, will consequently be in the reverse order: $a>b>c$. An "A" band shall be one in which the electric moment or change of moment is parallel to the minor or A axis, etc.

In the second place the energy levels of the unsymmetrical rotator are arranged in a most inconvenient fashion and it is not possible accurately to represent the positions and intensities of the rotation lines by simple functions of the moments of inertia.

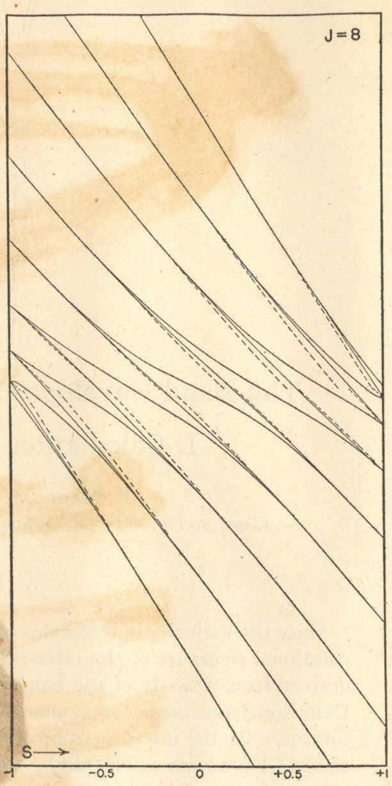

FIG. 1. The energy levels of an asymmetric rotator for $J=8$ plotted as a function of S, with $(a-c)$ and b kept constant. The continuous lines represent the levels given by the exact theory and the dashed lines indicate those given by approximate Eqs. (1) and (2). A horizontal line through the center of the figure would represent the energy $W_b=J(J+1)h^2b/8\pi^2$.

CALCULATION OF THE BAND ENVELOPES

Our first step in the calculation of the band envelopes was to find approximate expressions for the energy levels of the asymmetric rotator which are sufficiently accurate for our purposes and at the same time of a convenient form. These were obtained by an approximate solution of the secular determinant of Wang[4] using second-order perturbation methods.

In any particular case the secular determinant may be written in three different ways. To obtain reasonably accurate values for the energies with only second-order perturbation methods, it is necessary to use different forms depending on the energy ranges with which one is concerned. For levels with energy greater, or less, than $W_b=J(J+1)h^2b/8\pi^2$ the appropriate forms are those in which the diagonal terms are the same

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[4] S. C. Wang, Phys. Rev. 34, 243 (1929).

as they would be for symmetrical molecules with the reciprocals of the two like moments of inertia equal to the mean of b and c, or of a and b, respectively.

If one makes an approximation regarding the interaction terms by replacing $(J-\sigma)(J-\sigma+1)\times(J+\sigma)(J+\sigma+1)$ with $[J(J+1)-\sigma^2]^2$, one obtains general solutions for the two cases mentioned above, which may be written as follows:

$$W\approx(h^2b/8\pi^2)\left\{J(J+1)\left[1-\frac{\rho(5-3S)(1+S)}{8(3-S)}\right]+K'^2\frac{\rho(17-14S+S^2)}{8(3-S)}\right\}\quad\text{(Eq. (1)) for } W>W_b,$$

$$W\approx(h^2b/8\pi^2)\left\{J(J+1)\left[1+\frac{\rho(5+3S)(1-S)}{8(3+S)}\right]-K''^2\frac{\rho(17+14S+S^2)}{8(3+S)}\right\}\quad\text{(Eq. (2)) for } W<W_b,$$

where $\rho=(a-c)/b$ and $S=(2b-a-c)/(a-c)$, and K' and K'' are integers with maximum value J.

We prefer to take S as a measure of the symmetry of the molecule rather than Wang's b, since the latter quantity is not uniquely defined but may take three different values depending on how the determinant is written. It will be noted that S takes the values $+1$ for the symmetrical planar molecule, -1 for the symmetrical spindle, and O for those molecules which as regards arrangement of the energy levels we may regard as least symmetrical.

In restricting Eqs. (1) and (2) to their appropriate domains we may make use of an approximation suggested by an equation given in the second paper of Kramers and Ittmann.[5] For the lower limits of K' and K'' we may take $s'J$ and $s''J$, respectively, where

$$s'=(2/\pi)\tan^{-1}[(b-c)/(a-b)]^{\frac{1}{2}}$$

and $s''=1-s'$. The upper limit in each case is of course J.

As may be seen in Fig. 1, our approximation of the energy levels is entirely adequate except for a small "intermediate" region where the energy is not greatly different from W_b. On the scale to which the figure is drawn the levels calculated from Eqs. (1) and (2) cannot be seen to deviate from the actual ones up to the point at which the splitting becomes appreciable. From this point on they diverge along the dashed lines. Fortunately the failure of both equations in the transition region is not very serious. In the first place, only a small fraction of the energy levels are concerned. In the second place, the transitions involving levels in this region are the weakest in the cases where the predicted frequencies are most seriously in error, namely in the $\Delta J=\pm 1$ branches of the B type bands and the $\Delta J=0$ branches of the A and C type bands. In the remaining cases where the transitions are strong the approximation is not so poor.

In a rough first approximation of the band envelopes we have assumed that the transition probabilities are the same as those of the symmetrical rotator, using of course the rules which will be appropriate for the levels given by the two equations, respectively. This will lead to considerable error only in the "intermediate" region, as has been discussed by Dennison.[6] Since our energy expressions are of the same form as those for the symmetrical rotator the procedure which Gerhard and Dennison[7] have worked out is directly applicable and it does not seem to be necessary to give further details of our calculation except to mention two modifications which must be introduced. In the first place, two sets of calculations have to be made in each case taking account of the two regions of energy levels separately. In the second place, some changes have to be made in the limits of integration to take account of the fact that the lower limits of K' and K'' are $s'J$ and $s''J$, respectively.

Although this first approximation just described gives a reasonably satisfactory representation of the intensity distribution in either the $\Delta J=0$ or the $\Delta J=\pm 1$ branches of a band, the envelope obtained by combining the two may be considerably in error. It is easy to show that the sum of the transition probabilities between

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[5] H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **58**, 217 (1929).

[6] Randall, Dennison, Ginsberg and Weber, Phys. Rev. **52**, 160 (1937).

[7] The expressions given by Gerhard and Dennison contain several typographical errors and should not be used without careful examination.

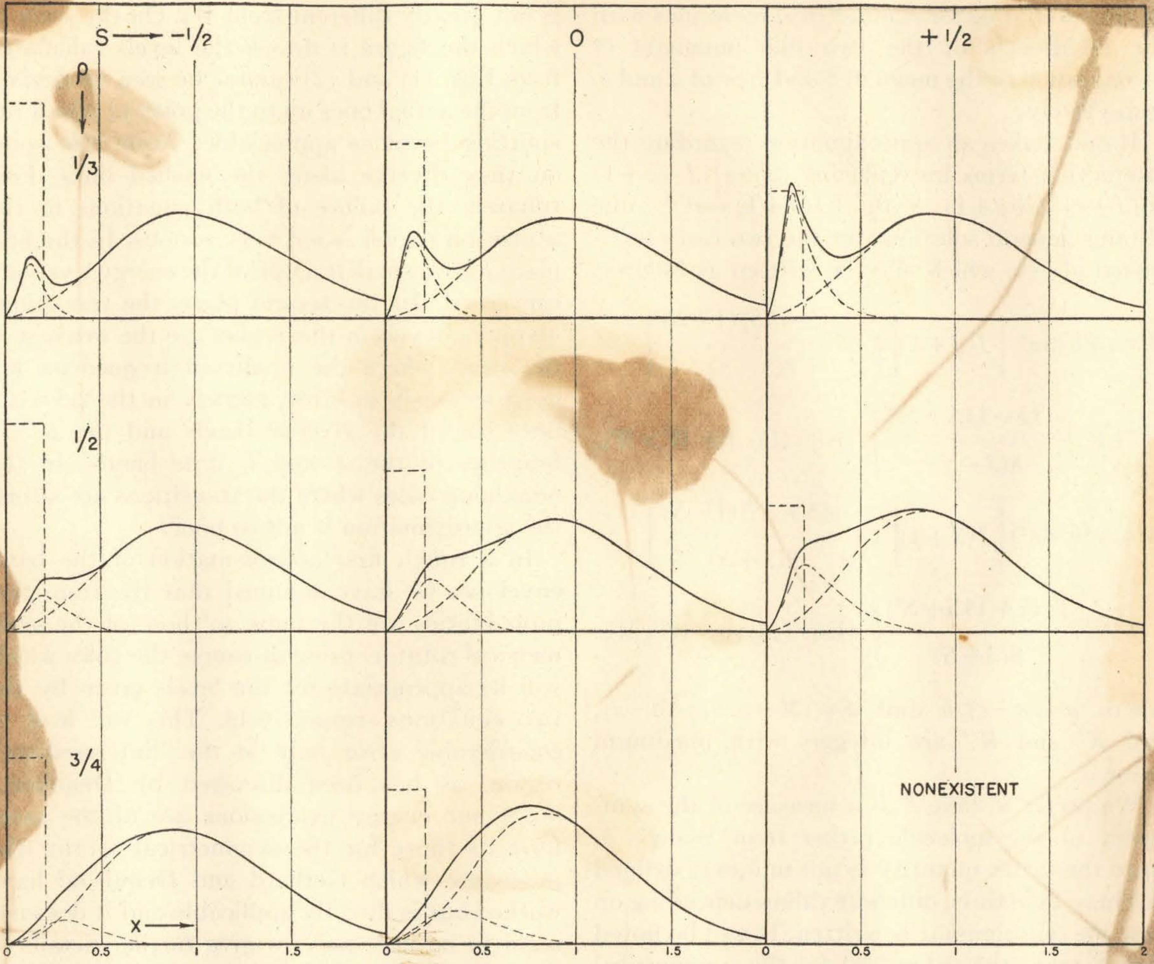

FIG. 2. The *A* bands (electric moment parallel to the minor axis of inertia) for eight different sets of parameters. The absorption coefficient is plotted as a function of *x*. One-half the band is shown, with the origin at the left. For further description see text.

levels of a given *J* value is independent of the symmetry of the molecule. Consequently this sum for any unsymmetrical molecule is the same as for the symmetrical rotator. A similar rule applies to transitions between levels which have *J* values differing by unity. In our approximation these rules are violated, though the ordinary sum rules are obeyed. This has the result that in the *B* type bands the branches with $\Delta J = 0$ are robbed of a considerable fraction of their intensity while the $\Delta J = \pm 1$ branches are augmented by the same amount. In the *A* and *C* type bands the errors are in the opposite direction and are less serious.

Since the symmetrical rotator intensity expression must hold fairly well for transitions between the highest and lowest energy levels, respectively, it is evident that these errors must arise from a serious failure in the intermediate region. Besides the failure with respect to the normal transitions there are of course additional transitions which have no analog in the symmetrical rotator case. We have found it difficult to estimate the total contribution of these, though general considerations seem to show that it cannot be large. We shall assume that it may be ignored, which seems to be justified by the observations on the rotation spectrum of water vapor. Out of a total of well over two hundred lines of sufficient intensity to be observed only eight could be identified as due to anomalous transitions, and none of these was very strong.[6]

Considering this assumption to be justified it is possible to apply a simple correction to the

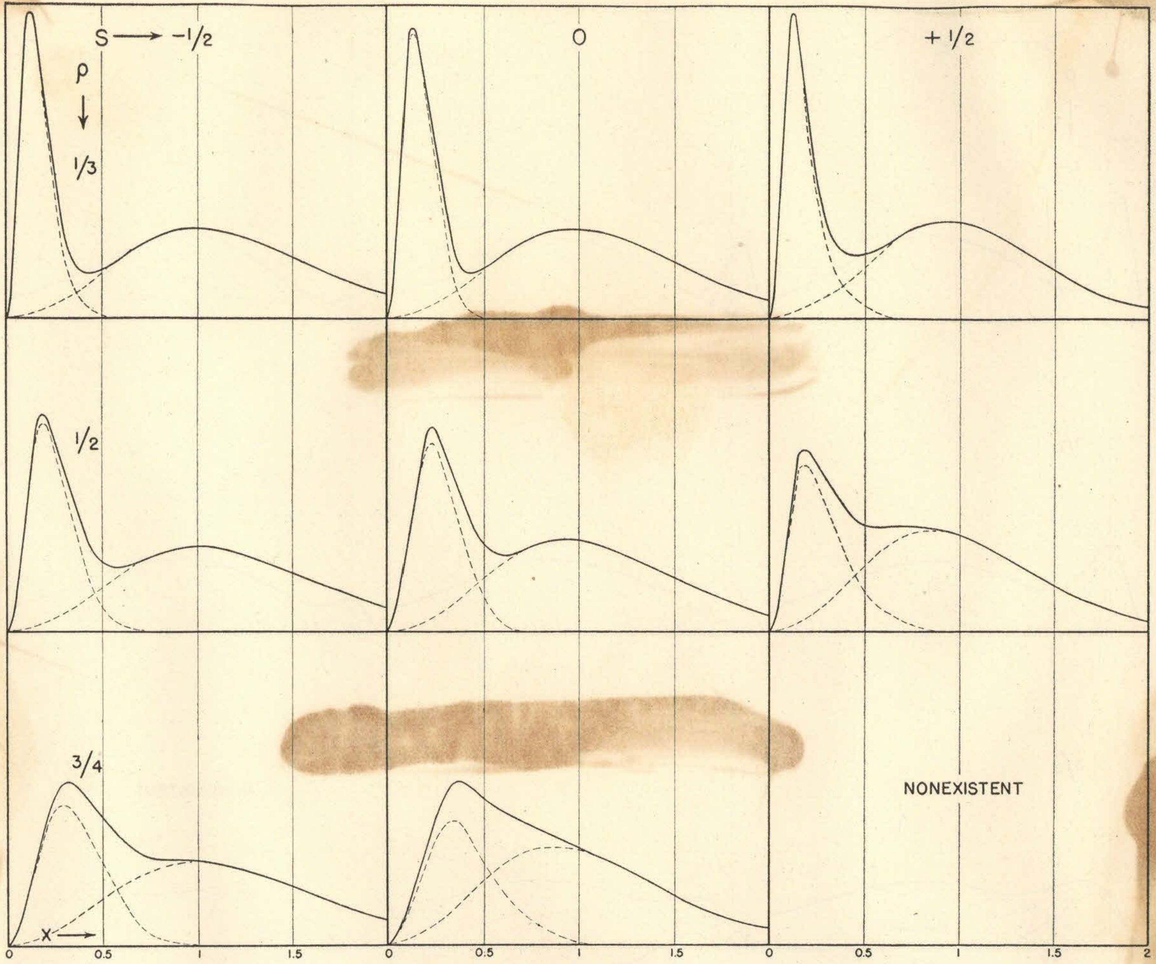

FIG. 3. The *B* bands (electric moment parallel to the intermediate axis of inertia).

band envelopes which takes into account the errors resulting from our approximation regarding the intensities. Actually of course we must expect that the symmetrical rotator expressions fit fairly well for the highest and lowest levels but fail more and more badly as one approaches the "intermediate" region. To compensate for this precisely would be difficult but it is simple to calculate two limiting envelopes between which the theoretically correct one should lie. In the one case one may assume that the intensity expressions are adequate except in the very center of the "intermediate" region where they abruptly fail, in the other case that they fail uniformly throughout.

In the former case the deficit or excess of the sum of probabilities for any set of transitions ($J \rightarrow J'$) may be accounted for by attributing it all to one transition in the very center of the "intermediate" region. Correction envelopes may then be calculated in a very simple manner, which have to be added to or subtracted from the envelopes obtained in our first approximation.

In the latter case the correction may be made by multiplying the probabilities of any given set of transitions by a constant factor. Since this factor is independent of J, one needs merely to multiply the ordinates of the $\Delta J = 0$ and the $\Delta J = \pm 1$ branches by the appropriate constants before adding them to obtain the total envelope.

It turns out that the corrected envelopes obtained by these two different procedures do not differ materially. This is, of course, to be expected since in any given set of transitions the probability changes rather rapidly from one line to the next and a small part of the total set is

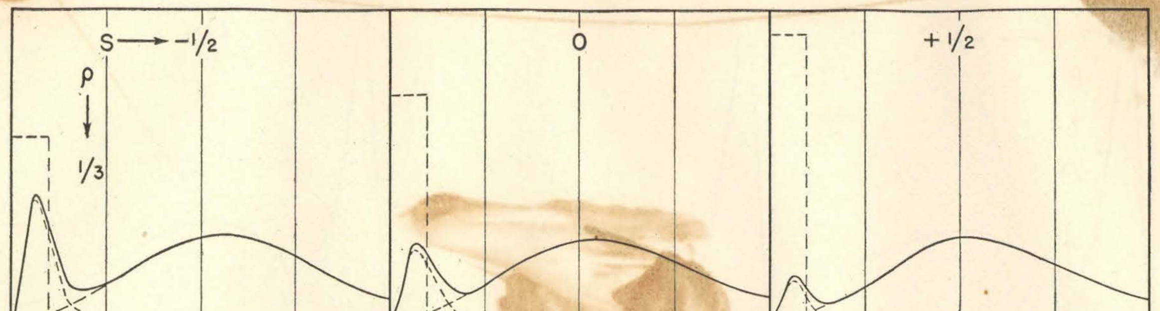

FIG. 4. The *C* bands (electric moment parallel to the major axis of inertia).

responsible for a large part of the intensity. Consequently we have been satisfied to calculate the envelopes by the second method and believe that they deviate less from the ideal theoretical ones than observed bands will normally do, owing to the nonrigidity of real molecules and other factors which we have not taken into account.

In Figs. 2, 3, 4 and 5 will be seen the three types of band envelopes for nine different sets of parameters. To save space only one-half the

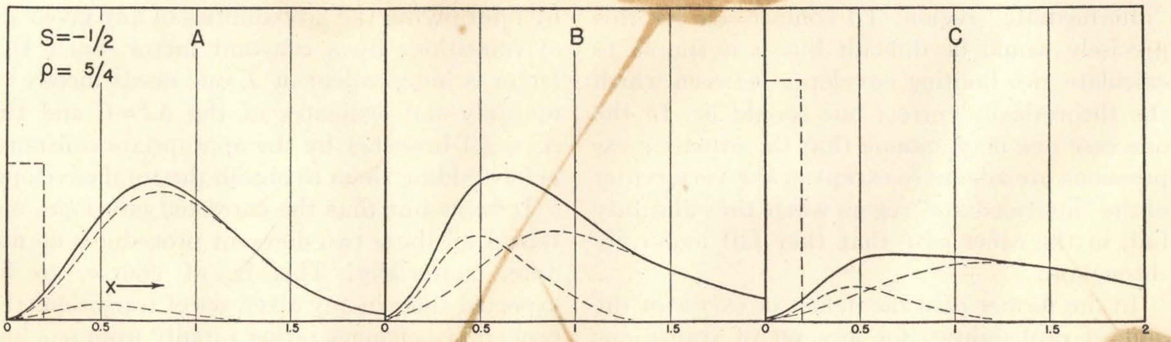

FIG. 5. The *A*, *B* and *C* bands for a molecule with $S=-\frac{1}{2}$ and $\rho=\frac{3}{4}$.

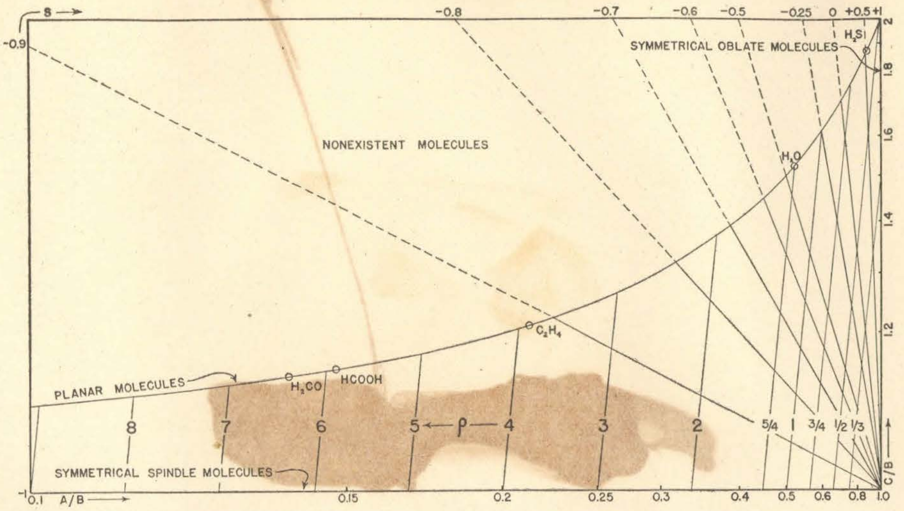

FIG. 6. Lines with constant S and with constant ρ plotted in a field with the dimensions a/b and c/b. The scales provided are in units of A/B and C/B rather than of the reciprocals.

band is shown in each case, with the origin at the left. The absorption coefficient has been plotted against x, where $x=(\nu-\nu_0)\pi(2B/kT)^{\frac{1}{2}}$, so that the figures are adaptable to molecules with any absolute moments of inertia and to any temperature. The frequencies are to be expressed in reciprocal seconds and B (the intermediate moment of inertia) and k in the usual units. The continuous lines represent the total envelopes while the dashed lines indicate the $\Delta J=0$ and the $\Delta J=\pm 1$ branches from which they are composed. In the A and C type bands the area of the dashed rectangle at the left represents one-half the amount of intensity in the collected "Q" branch. In the approximation to which we worked this branch should appear as a line of zero width. Actually this will not be the case, but in our experience the observed central branches have a width which is mainly due to the stretching of the molecule and to the difference in rotational constants in the normal and excited states and is much greater than would be expected for a rigid molecule with no interaction between rotation and vibration. In most cases this central branch can be well represented by a Gaussian function with width about $0.166x$ at half-height.

Our calculations have been confined to highly unsymmetrical and consequently little elongated molecules. These have been least investigated and seemed to us most interesting. The envelopes of spindle-shaped and slightly unsymmetrical molecules have become familiar through the investigation of several good examples.

Since one may wish to compare our curves with the envelopes of the "perpendicular" bands of the symmetrical rotator calculated by Gerhard and Dennison it may be worth while to call attention to the following facts. As S approaches $+1$ the A and B bands degenerate into perpendicular bands, which is likewise true of the B and C types when S approaches -1. In both limiting cases when $S=\pm 1$, $\rho S=-\beta$, where β is the parameter which Gerhard and Dennison have used to describe the symmetrical molecule.

Figure 6 may be of some assistance in the rapid estimation of the parameters S and ρ in any actual case. The lines of constant S and constant ρ are represented in a field with the dimensions a/b and c/b. For convenience the scales attached have been given in units of A/B and C/B, rather than of their reciprocals. Some molecules whose moments of inertia have been determined with some precision are located on the plot. It is of interest to note that in the extreme right portion of the figure the parameter S varies rapidly with the moments of inertia.

In a paper to follow we shall show how our calculated band envelopes have been of assistance in the interpretation of some observed bands.

An Absorption Band of Formaldoxime at λ 9572.

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An Absorption Band of Formaldoxime at λ9572*

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The third harmonic of the O—H band in formaldoxime vapor has been found to lie at λ9572 (10,444.1 cm^{-1}) and under high dispersion has been resolved and found to resemble a parallel band of a symmetric rotator. Owing to the weakness of the lines near the center of the band a definitely unique rotational analysis could not be made but the harmonic mean of the two larger moments of inertia appears to lie between the limits 73.3 and 76.6×10^{-40} g cm^2. The hydroxyl hydrogen does not rotate freely and indeed its torsional oscillation appears not to have a very low frequency. It is not possible to locate this hydrogen uniquely until other parameters of the molecule have been determined by electron diffraction. The possible effect of resonance on the O—H frequency is discussed.

EXPERIMENTAL

THE trimer of formaldoxime was prepared in the manner recommended by Scholl.[1] On heating the substance to around 100° it yielded the monomer in the vapor state. The formaldoxime vapor was confined in a ten-foot Pyrex absorption tube at about 100° and one atmosphere. Exploratory spectrograms were first taken with a glass spectograph of moderate dispersion to locate the O—H band. In the resolution of the rotational structure a 21-ft. grating was employed which has a dispersion of about 2.5A per mm in the first order. Eastman 144Q plates sensitized with ammonia were used and the wave-length calibration was made by means of iron lines in the third order.

EXPERIMENTAL RESULTS

As may be seen in Fig. 1, a single O—H band was found at λ9572 (10,444.1 cm^{-1}) with a simple structure apparently identical with that of a parallel band of a symmetrical molecule. In Table I are given the frequencies of the observed lines. These are the average of two independent sets of measurements. In the case of some of the

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* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, number 681.

[1] R. Scholl, Berichte **24**, 573 (1891).

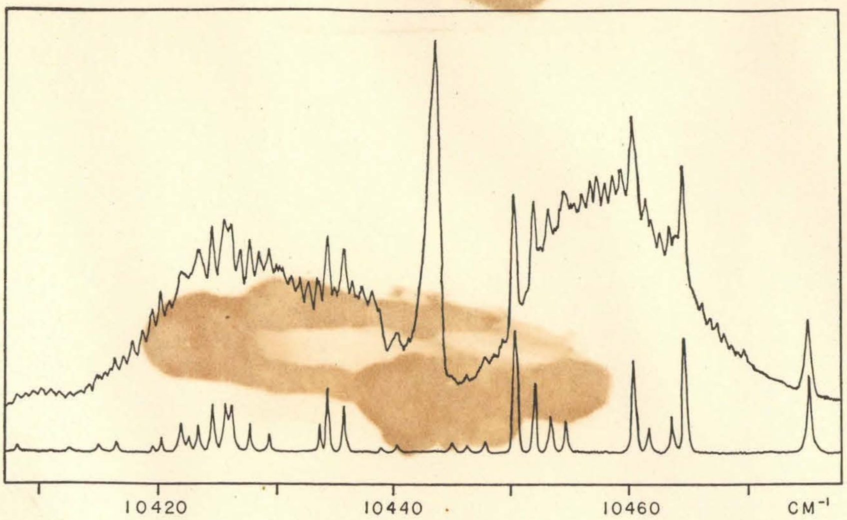

FIG. 1. Microphotometer curve of the O—H band at λ9572 in formaldoxime vapor. The water vapor spectrum in the same region is shown below.

weaker lines the error may be as large as 0.1 cm^{-1}. The separation of the maxima of the P and R branches is 31.0 cm^{-1}.

DISCUSSION OF THE RESULTS

Formaldoxime (H_2CNOH) appears to deviate rather little from being a symmetrical rotator both from considerations regarding its structure and from the appearance of the band here described. Consequently the spacing in this band will, for all practical purposes, be determined by the harmonic mean of the two nearly equal and larger moments of inertia. It should be possible then to evaluate this mean moment of inertia for both upper and lower vibrational states by making the same combinations which would be appropriate for a parallel band.

With the help of a Fortrat diagram J values were assigned to the lines. It was not possible to do this uniquely and in both P and R branches there are two assignments which appear to be equally plausible as shown in Table I. The combinations can consequently be made in four different ways. In obtaining the rotational constants from the combinations $\Delta_2F'(J)=R(J)-P(J)$ and $\Delta_2F(J)=R(J-1)-P(J+1)$, it was found convenient to plot $\Delta_2F''(J)/2(2J+1)$ against $(J+\frac{1}{2})^2$ since the effect of the stretching of the molecule with rotation is quite appreciable, and the extrapolation to the rotationless state would otherwise have been difficult.

The extreme values of the means of the two larger moments of inertia are those given by assignments 1 and 2 of Table I. They are, respectively, as follows: $D''=73.3\times10^{-40}$ and 76.6×10^{-40}, and $D'=73.6\times10^{-40}$ and 76.8×10^{-40}. There is a slight uncertainty in making the extrapolations but it appears very unlikely that the actual values of the moments of inertia should lie much outside the limits given.

TABLE I. *Frequencies of lines in the formaldoxime band at λ9572.*

ν (cm^{-1})	Alternative J Assignments No. 1	Alternative J Assignments No. 2
P branch		
10,411.12	42	43
11.75	41	42
12.49	40	41
13.33	39	40
14.13	38	39
14.91	37	38
15.58	36	37
16.32	35	36
17.10	34	35
17.83	33	34
18.59	32	33
19.35	31	32
20.13	30	31
20.88	29	30
—	—	—
26.88	22	22
27.67	21	21
28.46	20	20
29.23	19	19
—	—	—
31.15	17	17
31.86	16	16
32.61	15	15
33.42	14	14
34.21	13	13
—	—	—
P branch		
10,435.66	11	11
36.44	10	10
37.21	9	9
—	—	—
Q branch		
44.13		
R branch		
55.31	15	16
56.00	16	17
56.64	17	18
57.27	18	19
57.92	19	20
58.58	20	21
59.18	21	22
—	—	—
61.41	25	26
62.01	26	27
62.65	27	28
63.28	28	29
63.88	29	30
—	—	—
66.12	33	34
66.67	34	35
67.28	35	36
67.91	36	37
68.50	37	38
69.07	38	39

The Structure of Formaldoxime

Although it is not possible to determine the structure of formaldoxime from the data at present available, some interesting conclusions can be drawn. One of these is quite certain; the others may be somewhat in doubt and await further investigation for their confirmation. The appearance of the band at λ9572 seems to exclude completely the possibility of the free rotation of the hydroxyl hydrogen. The band appears to be simple in structure, and if there are any superposed bands arising from absorption from excited levels they are certainly quite weak. It appears reasonable to conclude that the O–H torsional vibration is not extremely low.

When hydroxyl hydrogen, though not free to rotate, may be found in more than one position of potential minimum, the O–H frequency appears to be considerably different in the different positions unless they correspond to equivalent or very similar configurations of the molecule. The fact that only one O–H band is observed at λ9572 may be taken as indicating that in the great majority of molecules at least the hydroxyl hydrogen is to be found in only one definite position, which one would consequently expect to correspond to a rather deep potential minimum. Since the molecule is most probably planar, it is of interest to speculate as to which of the two geometrically possible plane configurations is the more probable.

In both models the O–H bond makes a considerable angle with the minor axis of the molecule and if the change in electric moment is more or less parallel to this bond it is a little difficult to see how either can give rise to hydroxyl bands so predominantly "parallel" in character as the one observed. However, the one represented in Fig. 2 in which the hydroxyl hydrogen is farthest removed from the carbon atom seems definitely to be more probable.

The moments of inertia of the molecule would be of assistance in locating the hydroxyl hydrogen if the other parameters were known. Some of them can be estimated with sufficient accuracy but since there seems to be some possibility of resonance in formaldoxime one hesitates to make a guess as to the C–N and N–O distances. The latter is particularly uncertain, and the assistance of electron diffraction measurements must be awaited.

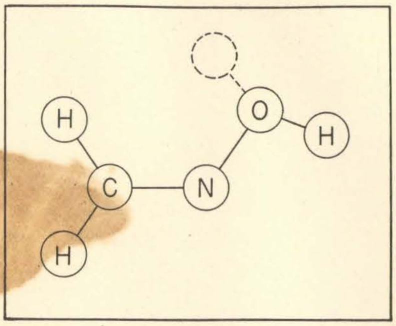

Fig. 2. Possible configurations of the formaldoxime molecule. The less probable location of the hydroxyl hydrogen is shown by dotted lines.

If the N–O bond does have appreciable double bond character, one should expect the O–H frequency to be somewhat affected, probably lowered. An effect of this sort may well be responsible for at least a part of the lowering of the O–H frequency in the carboxylic acids and in nitric acid. Indeed it is possible that the frequency lowering might serve as some measure of the importance of the resonance and it is unfortunate that internuclear distances are not available in any cases which might serve for calibration. However, it is doubtful whether any simple relation exists owing to the presence of numerous other complicating factors.

The third harmonic O–H band of formaldoxime has nearly the same frequency as the analogous one of phenol. In the latter molecule the importance of resonance has already been suggested.[2] In both cases the frequency is indeed slightly lower than in the primary alcohols but may still be regarded as well within the normal range. Consequently it appears unlikely that the N–O and C–O distances in the two molecules, respectively, will be found to be much shorter than the normal single bond distances. Electron diffraction measurements will, however, be awaited with interest.

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[2] L. Pauling, J. Am. Chem. Soc. 58, 94 (1936).

Investigation of the Third Harmonic O-H Bands of Substituted Alcohols.

Investigation of the Third Harmonic O-H Bands of Substituted Alcohols.

Prefatory Remark

In the following paragraphs will be described a spectrographic investigation which definitely comes in the domain of chemistry rather than physics. The molecules studied appear to be much too complicated to be given a quantum mechanical treatment in order to correlate the details of the observed spectra with the formalism of physics. However, the results of the experiments can be at least partially understood in terms of the concepts of structural chemistry and add a little more to our knowledge concerning intramolecular hydrogen bond formation.

Introduction

In the last few years the O-H harmonic bands of alcohols and phenols have been studied and it has been observed that they may be split up into two or more components. Pauling[1] has offered a satisfactory explanation of the splitting of the O-H frequency in the case of o-chlorophenol. The two observed bands are said to correspond to two different forms of the o-chlorophenol molecule. In one form the hydroxyl hydrogen lies in the plane of the benzene ring and is at the distance of closest approach to the ortho chlorine atom. In the other form the hydroxyl hydrogen lies in the plane of the ring but is on the side away from the chlorine atom. The frequency of the O-H valence vibration in the case of the latter form is about the same as the O-H frequency of phenol while in the case of the first configuration the O-H frequency is somewhat lower. Pauling points out that the hydroxyl hydrogen atom when near the electronegative chlorine atom will undergo an attractive interaction, i.e. form a hydrogen bond, and this has the effect of lowering the O-H vibrational frequency.

Badger and Bauer[2] in considering the doublet band characteristic of the O-H harmonic bands of the vapors of normal alcohols have suggested that the alcohol molecule may exist in two forms which correspond to slightly different O-H frequencies.

The splitting of the O-H frequency arising from the presence of an adjacent halogen group in the case of alcohols was observed by Barchewitz and Freymann[3]. These workers obtained the absorption spectra of pure liquids and their solutions in inert solvents. Since in the liquid state one will have hydrogen bonds formed between alcohol molecules and also interaction with the inert solvent, it has been considered worth while to investigate the infrared absorption spectra of the vapors of substituted alcohols. The smaller number of factors having a bearing on the absorption spectra of a vapor as compared to a liquid allows us to obtain more definite knowledge relating to intramolecular hydrogen bond formation if we study the absorption spectra of substituted alcohols in the vapor state rather than in the liquid state.

Ordinarily the different forms of the alcohol and phenol molecules will have somewhat different energies. Under these circumstances the relative intensities of the component O-H bands which correspond to the different molecular configurations should change with temperature. An investigation of this point forms an important part of this study.

Compounds Studied

The propyl alcohol studied was obtained by fractional distillation from Eastman "practical" normal propyl alcohol. The boiling point of the purified product was 97.2°C (corrected to 760 mm. Hg.). Eastman ethylene chlorohydrin was redistilled the product having a boiling point of 128.8°C (corrected to 760 mm.). Trimethylene chlorohydrin prepared by Mr. M. J. Schlatter in these laboratories was used without further treatment. Propylene chlorohydrin, ethylene bromohydrin and trimethylene bromohydrin, all Eastman products were investigated without further purification. Their refractive indices were found to be $n_D^{20.6°} = 1.4370$, $n_D^{20.5°} = 1.4926$ and $n_D^{24.5°} = 1.4885$ respectively. Sym-glycerol dichlorohydrin (Eastman) which was of the practical grade had an index of refraction of $n_D^{20.5°} = 1.4830$. This compound was distilled under reduced pressure and the middle fraction was used in the spectroscopic investigation. The methyl cellosolve (2-methoxy-ethanol), a product of the Mefford Chemical Co., was distilled and had a boiling point of 124.1° (corrected to 760 mm.). The o-chlorophenol (Eastman) used in the experiments boiled at 174.3° (748 mm. Hg.) An investigation of the boiling points of o-chlorophenol under reduced pressures gave the entropy of vaporization at the boiling point as 21.9 cal./deg.[*]mole

Apparatus and Experimental Procedure

This investigation was carried out with the use of a Littrow glass spectrograph with a dispersion of about 70 A per mm. at λ 9000. Eastman 144Q and 1Z infrared plates were used. These plates were hypersensitized with aqueous ammonia and dried using methyl alcohol. A comparison spectrum of barium lines was placed on each plate. The values found for the frequencies of the centers of the absorption bands are accurate to about 5 cm^{-1}. Some uncertainty arises in the estimation of the true maxima of the bands in making comparator measurements.

A three meter Pyrex absorption cell which was held in a resistance furnace consisting of a sheet metal tube wrapped with asbestos and iron wire was employed. The resistance furnace was of somewhat greater length than the cylindrical absorption cell and had one lens at each end placed intermediate between the end of the furnace and the cell. The pressure of the vapor in the cell was regulated by fixing the temperature of a trap which held an excess of the liquid and which was connected to the bottom of the absorption cell at one end.

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[*] Note: using the same apparatus the entropies of vapori- at the boiling point, of phenol (reagent quality) and p-chlorophenol (Eastman) were evaluated as 24.7 and 24.4 cal./deg.mole respectively.

The absorption spectra of the substances were obtained at pressures of about one atmosphere.

Microphotometer curves for the bands of each alcohol were obtained as well as the curves for plates exposed when the absorption cell was filled with water vapor and when the absorption cell was empty. The latter were taken to get the positions and shapes of the water absorption bands (which might be superimposed on alcohol O-H bands) and to get the curve corresponding to background blackening. The sensitivity of the 144-Q plates changes very markedly with wave-length in this region, and thus the background blackening changes considerably with wave length.

Results of Studies on the Substituted Alcohols

The absorption maxima of the substituted alcohols studied are listed in Table I. Figure 1 gives the microphotometer curves of the O-H third harmonic bands of these alcohols. The microphotometer curves are uncorrected for change in plate sensitivity with wave-length. The dashed line below the curves indicates the trend of the background blackening. The different observed trends correspond to different batches of plates used. The only appreciable water vapor absorption occurs always at frequencies a little higher than those of the alcohol O-H vibrations. The ordinates of the microphotometer curves do not have any absolute significance as they were obtained with differing microphotometer settings, plate blackenings, and concentrations of the absorbing substance.

Table I

Absorption maxima in the O-H third harmonic bands of the vapors of seven substituted alcohols

Substance	Synonym	Formula	Absorption maxima (cm^{-1})
Ethylene chlorohydrin	2-chloro-ethanol	$ClCH_2CH_2OH$	10,367 10,485 10,546
Ethylene bromohydrin	2-bromo-ethanol	$BrCH_2CH_2OH$	10,318 10,470 10,527
Methyl cellosolve	2-methoxy-ethanol	$CH_3OCH_2CH_2OH$	10,384 10,472 10,538
Trimethylene chlorohydrin	3-chloro-1-propanol	$ClCH_2CH_2CH_2OH$	10,467 10,525
Trimethylene bromohydrin	3-bromo-1-propanol	$BrCH_2CH_2CH_2OH$	10,470 10,529
Propylene chlorohydrin	1-chloro-2-propanol	$ClCH_2CHOHCH_3$	10,326 10,460
Sym-glycerol dichlorohydrin	1,3-dichloro-2-propanol	$ClCH_2CHOHCH_2Cl$	10,243 10,325

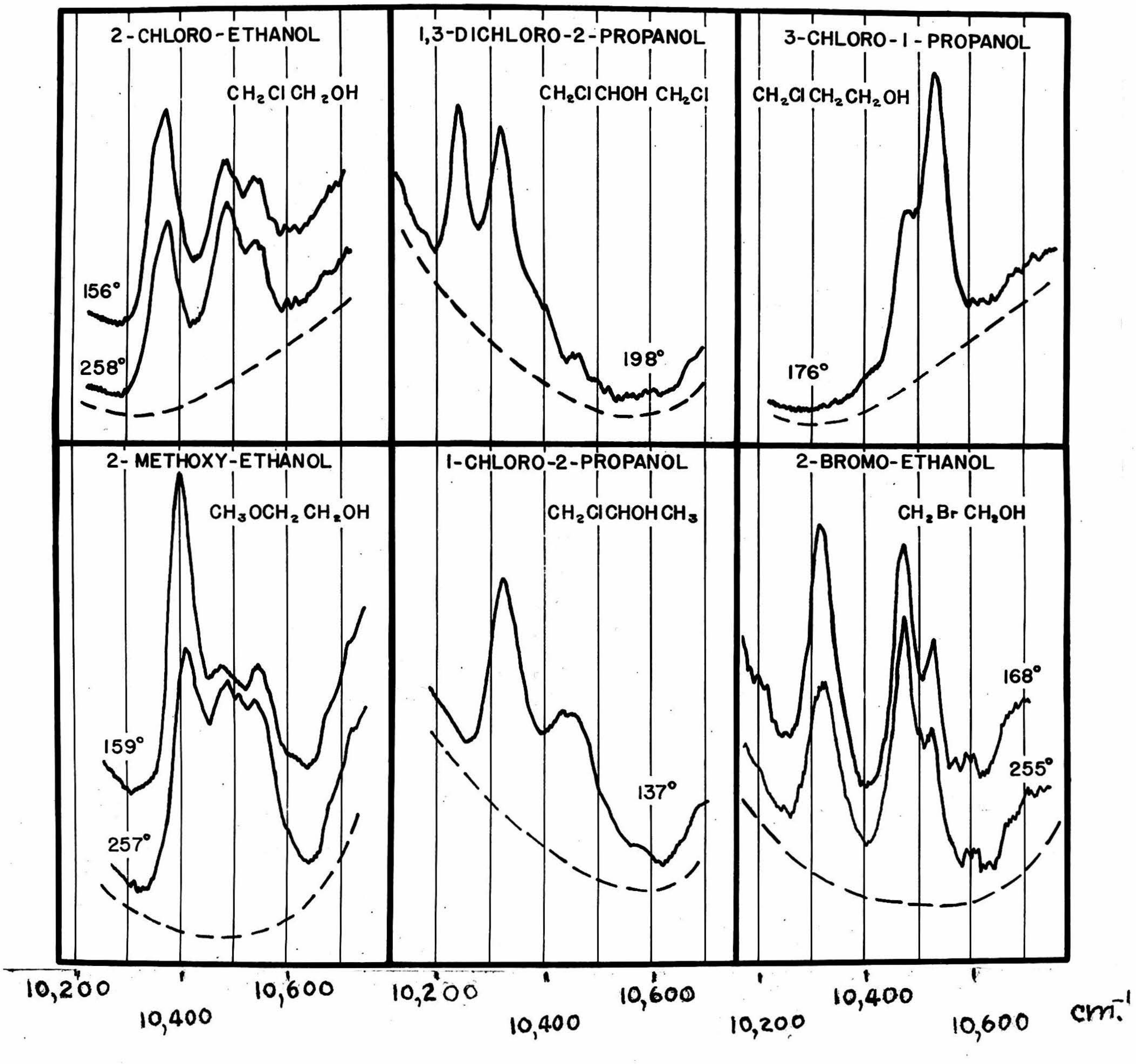

Figure 1. Microphotometer curves of the O-H third harmonic absorption bands in the vapors of six substituted alcohols. The temperature of the vapor is marked on the curves.

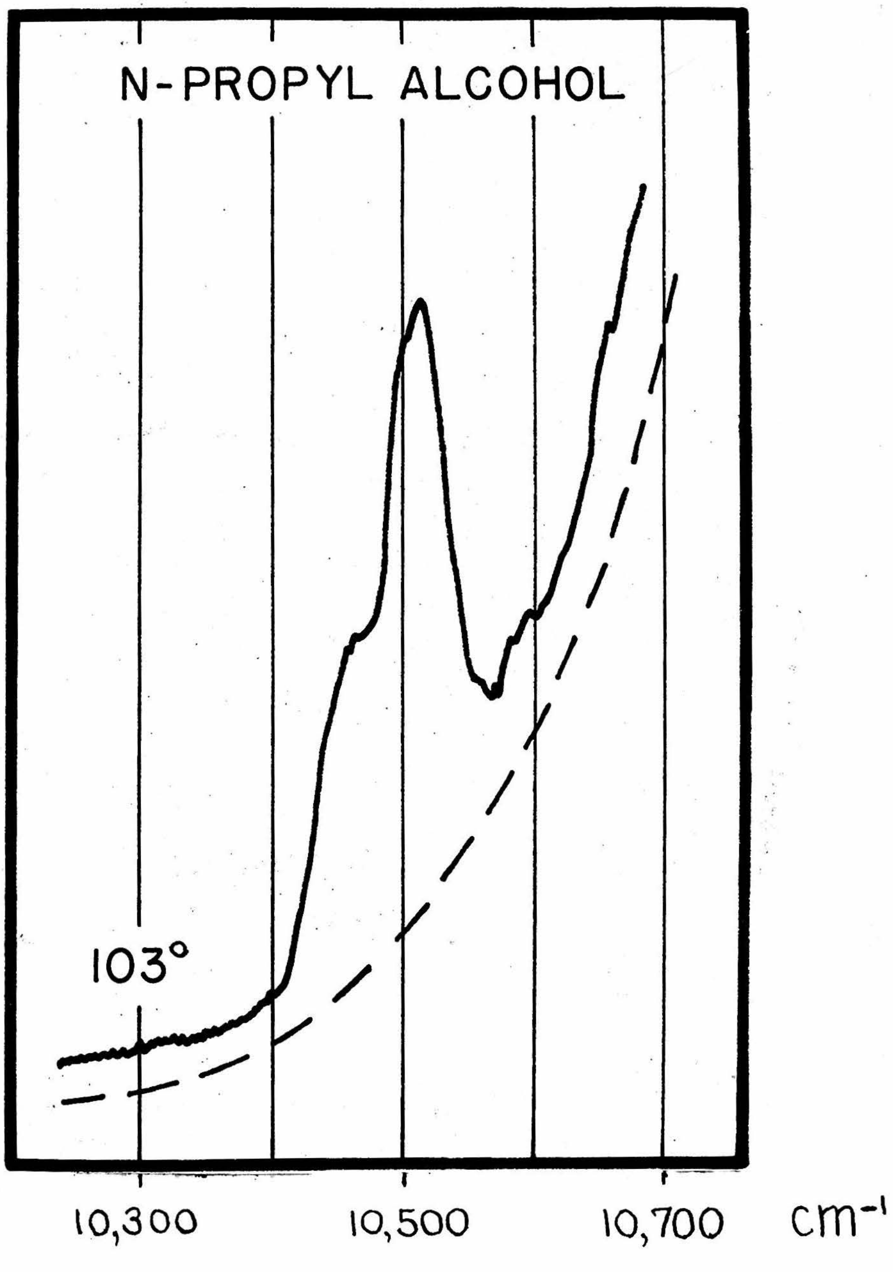

Figure 2. Microphotometer curve of the O-H third harmonic absorption band of n-propyl alcohol. The dashed line indicates the trend of the background blackening.

Substituted ethanols

If we compare the above data on ethylene chlorohydrin, ethylene bromohydrin and 2-methoxy-ethanol with the data of Badger and Bauer[2] we find that we still have the doublet band characteristic of normal alcohols (displaced to slightly higher frequencies); however, we also have a new band appearing at a frequency of around a hundred wave numbers lower. This new band would seem to arise from a situation analogous to that occurring in orthochlorophenol.

Let us consider ethylene chlorohydrin. Here, we have a hydroxyl group and a chlorine atom attached to different but adjoining carbon atoms, as in the case of orthochlorophenol. The geometrical situation is a little different in the two cases on account of somewhat different angles and internuclear distances, but it would seem probable that an intramolecular hydrogen bond could be formed between the chlorine atom and the oxygen atom in ethylene chlorohydrin. In such a case there would be a chelation to form a five-membered ring. An explanation for the occurrence of the observed bands can be that the new low frequency band, which appears in the case of the substituted alcohol, corresponds to configurations of the molecule wherein the hydroxyl hydrogen forms a hydrogen bond with the chlorine atom. The O-H frequency for these configurations of ethylene chlorohydrin is lower than the normal O-H frequency because of the attractive interaction of the hydroxyl hydrogen and chlorine atoms. The higher frequency doublet band corresponds to configurations of the molecule in which the hydroxyl group is in a situation similar to that in which it finds itself in the unsubstituted alcohol.

The nature of the O-H bands in the cases of ethylene bromohydrin and 2-methoxy-ethanol is thought to be quite the same as in the case of ethylene chlorohydrin. The low frequency band corresponds, in each instance, to a form of the molecule which is chelated. In ethylene bromohydrin a hydrogen bond joins the oxygen and bromine atoms. In 2-methoxy-ethanol a hydrogen bond joins the two oxygen atoms of the molecule.

As is shown in Fig. 1 the relative intensities of the bands of the three substituted ethanols change markedly with temperature. The intensity of the low frequency O-H band decreases with temperature, while the intensity of the doublet band increases with temperature. According to Boltzmann's principle, the high energy states become more populated as the temperature is raised. This principle when applied to the above observation indicates that the molecular forms corresponding to the low frequency O-H band have a lower potential energy than the molecular forms corresponding to the doublet band. The chelated form of the substituted alcohol, thus, has the lowest energy of all the molecular configurations. We might well expect this, for, in general, the formation of a hydrogen bond involves a potential energy decrease of several kilocalories per mole.

The change, with temperature, in the relative intensities of the bands of these three substituted ethanols would rule out the idea that the new band appearing in the substituted alcohol spectrum is a combination or harmonic band other than the third harmonic O-H band, for if these bands all involve transitions from the ground state, one would observe no effect of temperature on the relative intensities of the bands. If the new band originated from a low lying excited state of the molecule, the intensity of this band would increase with temperature, however, the intensity of this band actually decreases with temperature.

Sometimes, in molecular spectroscopy, one observes weaker bands on the low frequency side of a main band which are due to transitions in which, in both the upper and the lower state corresponding to the main band, a low frequency vibration is excited. Methyl acetylene[4] furnishes an example of this phenomenon. In such a case, however, the intensity of the low frequency band increases with temperature, and furthermore a series of equally spaced low frequency bands appear. The ratio of intensities of the first low frequency band and the main band is about equal to the ratio of intensities of the second and first low frequency bands. The bands become successively less intense. Consideration of the observed bands of the substituted ethanols quickly rules out this last mentioned possible explanation for the observed new low frequency band.

It is perhaps worthwhile to note that the ratio of intensities of the components of the doublet band in the case of these substituted ethanols is almost the inverse of the ratio in the case of ethanol[2]. No obvious reason for this has suggested itself. One further notices that the band corresponding to a chelation occurs at a lower frequency in the case of ethylene bromohydrin than in the case of ethylene chlorohydrin. This brings to mind the studies of Wulf, Liddel and Hendricks[5] who observed that the intense band corresponding to the cis form of the orthohalogenophenols occurred at progressively lower frequencies in the order o-chloro-, o-bromo-, and o-iodophenol. The increased frequency separations can be attributed to greater hydrogen bond interaction which is possible on account of the increased size and thus closer approach of the halogen atom when halogen atoms of progressively increasing molecular weight are placed on the ortho position. Nevertheless, it is not impossible to have a situation in which closer approach to the halogen atom would lead to a decrease in frequency shift on account of a repulsive interaction setting in. Presumably this is not the case.

Substituted Secondary Alcohols

Propylene chlorohydrin has the rather broad band with a single maximum, which is characteristic of unsubstituted secondary alcohols, and in addition a narrower band at a somewhat lower frequency. This is analogous to the phenomenon observed in the case of the substituted ethanols, i.e., a new low frequency band appears in the absorption spectrum of the substituted alcohol. Similarly the low frequency band is thought to be characteristic of a molecular form of propylene chlorohydrin in which there is an oxygen-chlorine intramolecular hydrogen bond.

Sym-glycerol dichlorohydrin possesses two sharp absorption bands with maxima at 10,243 and 10,325 cm^{-1} and, perhaps, a trace of absorption in the region characteristic of unsubstituted secondary alcohols. We suggest that the 10,325 cm^{-1} band, as in propylene chlorohydrin, corresponds to a configuration where the hydroxyl group forms a hydrogen bond with one of the chlorine atoms, while the 10,243 cm^{-1} band corresponds to a configuration where the hydroxyl hydrogen is able to interact with both chlorine atoms. In the latter situation we have a double ring chelation.

Trimethylene Chlorohydrin and Trimethylene Bromohydrin

Let us briefly consider the possible three dimensional configurations of trimethylene chlorohydrin. Present knowledge of structural chemistry indicates that rotation about the carbon-carbon single bond is restricted. The equilibrium orientation of one carbon with respect to rotation about the bond joining it to another is, however, unknown. There are two plausible structural arrangements with respect to relative rotation about the C-C bonds; so in discussing the structure of a molecule which contains carbon-carbon bonds, it is necessary to consider both arrangements. The two plausible forms will be, here, denoted by h and d. The h-configuration corresponds to the situation where the orientation of each carbon atom is such that a plane passing through the bond connecting a pair of carbon atoms and passing through one of the remaining tetrahedral bonds of one of the carbon atoms will pass through a tetrahedral bond of the other carbon atom. The d-configuration corresponds to the molecular form obtained from an h-configuration by making a rotation of 30° about each carbon-carbon bond.

The distance between the oxygen and chlorine atom for a given configuration of trimethylene chlorohydrin should have an important bearing on the strength of a hydrogen bond between these atoms. For example, chelation is entirely impossible in the case of the h-configuration of trimethylene chlorohydrin where the oxygen, chlorine and the three carbon atoms all lie in a plane because the oxygen-chlorine distance (1.68 A[x]) is so small that only a repulsive interaction could occur. The oxygen-chlorine distance for other forms of the molecule which conform to the h-configuration is too great for one to expect hydrogen bond formation. A twisting about the C-C bonds, which supposedly leads to a potential energy increase, would be required to bring the chlorine and oxygen to a distance more favorable for hydrogen bond formation. In the d-configuration, the oxygen-chlorine distance (2.53 A[x]) would seem to be a little small for hydrogen bond formation. The distance

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[x] Internuclear distances calculated assuming the tetrahedral bond angles and the normal single bond covalent distances.

in the case of o-chlorophenol, where we have a relatively strong hydrogen bond, is 2.98 A. One would certainly expect the oxygen-oxygen distance for a strong hydrogen bond to be less than the oxygen-chlorine distance for an equally strong hydrogen bond since the chlorine atom has a greater radius than the oxygen atom. In dimeric formic acid, where we have strong hydrogen bonding, the oxygen-oxygen distance is 2.67 A^{o}. It would seem that an oxygen chlorine distance of 2.53 A is too small for a good hydrogen bond. A twisting about the carbon-carbon bond will lead to a more favorable oxygen-chlorine distance, but this may have the effect of counter balancing the decrease in the potential energy of the molecule due to formation of a stronger hydrogen bond by tending to increase the potential energy on account of rotation about the carbon-carbon bonds. The increase of energy due to twisting would not amount to more than three or four kilocalories per mole; hence such a "strained" chelated configuration should not have an energy much higher than that of other possible configurations. The chelated molecules should therefore have an appreciable existance at ordinary temperatures and should show up in the absorption spectrum provided the fraction of chelated configurations relative to all possible configurations is not too small. Although there will be a greater number of configurations wherein there is no chelation relative to the number of configurations where there is chelation in the case of the trimethylene halogenohydrins than there will be in the case of the substituted

alcohols
/previously discussed, it would seem that there should be an appreciable fraction of chelated forms in the former case.

According to the above it might be anticipated that one would obtain spectroscopic evidence of chelation to form a six-membered ring in the case of trimethylene chlorohydrin and trimethylene bromohydrin. The microphotometer curves, however, do not give evidence of an additional component O-H band of somewhat lower frequency than the normal doublet band.

Temperature Effect Investigation

A photometric investigation of the effect of change in temperature on the bands of normal propyl alcohol, ethylene chlorohydrin, and orthochlorophenol was made. The experimental procedure is the following. The temperature of the absorption cell was held constant by fixing the voltage across the resistance furnace and the temperature was read from a thermometer inserted in a well at the midsection of the absorption cell. It is estimated that the corrected thermometer reading gave the temperature of the absorbing vapor within three or four degrees.

Having fixed the temperature of the vapor of the absorbing substance, the absorption spectrum of this compound was taken at a series of different vapor densities of the substance. The pressure of the vapor was fixed by maintaining the temperature of the trap connected to the absorption tube at a constant value. This temperature was always lower than the temperature of the absorption cell and an excess of liquid was held in the trap. With this arrangement whenever equilibrium is established one knows that the pressure of the vapor in the absorption cell is equal to the vapor pressure of the liquid in the trap. The system was allowed to stand at a fixed temperature for over an hour before an exposure was made in order to insure the attainment of equilibrium. In the case of the o-chlorophenol experiments the temperature of the liquid in the trap was fixed by employing a well agitated oil bath which could be kept at a temperature which was constant within two-tenths of a degree.

The first part of the series of exposures, each of which corresponded to a definite vapor density, was taken with the temperature of the vapor in the absorption cell a little above the temperature corresponding to the boiling point of the substance. Then exposures were taken with the temperature of the vapor seventy-five or one hundred degrees higher. All of the exposures were taken with an equal exposure time and with equal intensity of the light source. When the temperature of the absorption cell was brought from the lower temperature to the higher temperature, there was a tendency for the part of the optical system which was held in the resistance furnace to become slightly displaced on account of thermal expansion. This necessitated a compensating adjustment of the mirror directing the beam of light to the slit of the spectrograph. All exposures of any such series were taken on the same photographic plate. This is important because then all exposures of a series are made on a photographic plate of the same sensitivity and are subjected to identical conditions of photographic development. The equal exposure times, equal intensity of illumination of the slit, equal conditions of sensitivity and development lead to a uniformity in the photographic image of the spectrum which is essential for the photometric method employed.

Microphotometer curves of the absorption spectrum corresponding to each of these exposures were obtained keeping the microphotometer sensitivity and zero settings the same through - out. The microphotometer employed was a Krüss instrument of the Koch-Goos type. The goal of uniform exposure was not completely attained, as the background blackening was shown by the microphotometer to vary somewhat. This was probably largely due to the fact that in readjustment of the mirror after the beam had been slightly displaced the slit was not illuminated exactly the same as before. It is believed that the difference in background blackening in a given series of exposures is not great enough to invalidate the photometric method which will be described in the next section.

Photometric Studies

Figure 3 gives a typical pair of microphotometer curves which show the effect of change in temperature on the intensity of the third harmonic O-H absorption bands of o-chlorophenol. We will now describe the photometric method of studying the effect of temperature on these bands. The photometric experiments are carried out as described above. Each exposure on the plate corresponds to an absorption spectrum of o-chlorophenol vapor which is at a given pressure and at a given temperature. The microphotometer deflections corresponding to each of the two absorption bands (A band at 10,443 cm^{-1} and B band at 10,189 cm^{-1}) are measured from the microphotometer trace of each absorption spectrum photograph. The measure-

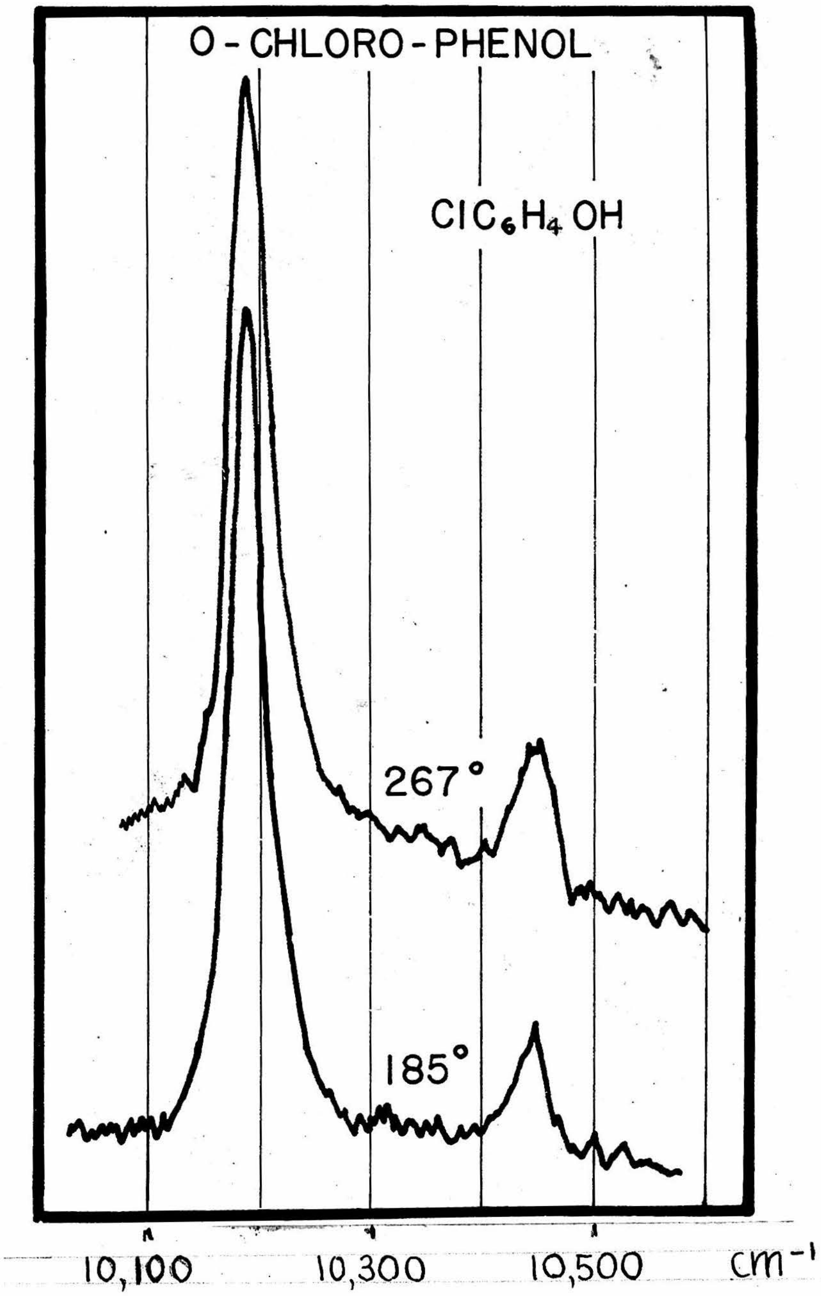


Figure 3. Microphotometer curves of the O-H third harmonic absorption bands in the vapor of o-chlorophenol at two different temperatures.

ment of the microphotometer deflection consists of measuring on the microphotometer trace the heighth of the peak of the absorption band above the line corresponding to background glackening (no absorption). The microphotometer deflections $(D_A)_{T_1}$ and $(D_B)_{T_1}$ corresponding respectively to the A and B bands, for all the exposures made when the o-chlorophenol vapor was at the temperature T_1 are plotted on the same graph against the pressure of the vapor. An example of such a plot is given in Figure 4.

Let $(D_A)_{T_2}$ and $(D_B)_{T_2}$ be values of the microphotometer deflections for an exposure taken when the o-chlorophenol vapor was at the temperature T_2 and let P_x be the pressure which corresponds to the value $(D_A)_{T_1} = (D_A)_{T_2}$ on the $(D_A)_{T_1}$- pressure curve plotted from data obtained at T_1. Likewise let P_y be the pressure which corresponds to the value $(D_B)_{T_1} = (D_B)_{T_2}$ on the $(D_B)_{T_1}$-pressure curve plotted from data obtained at T_1. If certain reasonable assumptions hold, then, it follows that

$$\Delta E^\circ = E^\circ_A - E^\circ_B = \frac{T_1 T_2}{T_2 - T_1} R \ln \frac{P_x}{P_y} \qquad (1)$$

where ΔE° is the difference in the thermodynamic molal internal energy at standard conditions of the two molecular forms corresponding to the A and B bands and where R is the molal gas constant. By finding the values of P_x and P_y from the microphotometer traces corresponding to exposures taken at T_1 and T_2 and using formula (1), ΔE° was evaluated.

The principal assumption upon which the above formula is based is that the microphotometer deflection corresponding to either one of the bands for a series of exposures taken on

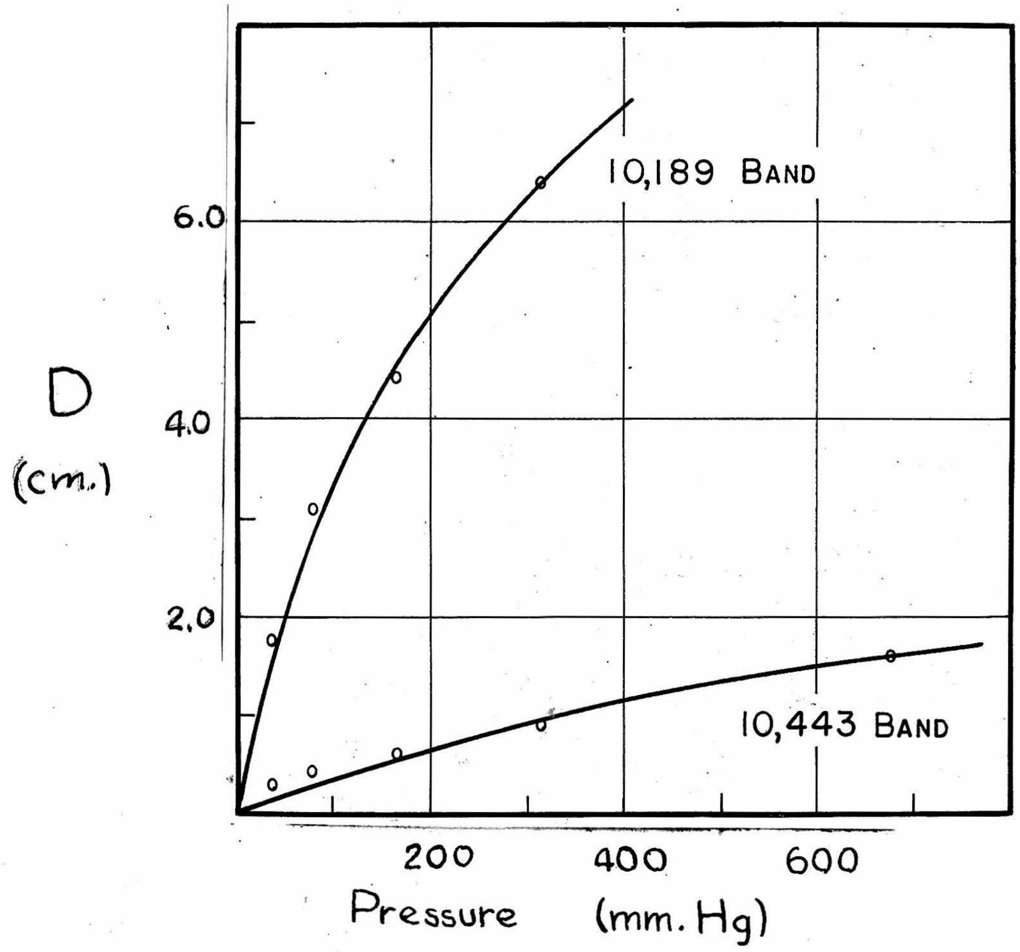


Figure 4. Plot of the microphotometer deflections corresponding to the A band (10,443 cm^{-1}) and the B band (10,189 cm^{-1}) in the vapor of o-chlorophenol versus the total pressure of the vapor. The data was obtained from a series of exposures taken on the same photographic plate and during each exposure the vapor was at a constant temperature T_1.

the same plate is solely a function of the number of molecules in the absorption cell which are in the configuration corresponding to the band under consideration. The microphotometer deflections should be independent of the intensity of the source of radiation, length of path of absorbing vapor, illumination of the slit and the exposure time since these possible variables are held constant throughout a series of exposures. Since all exposures are taken on the same photographic plate, there should be uniform sensitivity of the emulsion and uniformity in the development of the photographic images corresponding to the absorption spectra. Furthermore, in obtaining microphotometer traces of the absorption bands the zero and the sensitivity of the microphotometer is kept constant while obtaining the records of bands for the entire series of exposures on a given plate. As a result, the behavior of the microphotometer should be unchanging and the position of the recorded image of the quartz fiber of the microphotometer electrometer should only depend on the density of silver in the photographic image of the absorption spectrum. A quantity which can affect the observed microphotometer deflection is temperature, for, if an absorption band becomes broader at a higher temperature of the vapor but retains its original intensity, it will have a smaller microphotometer deflection, i.e. the vertical distance on the microphotometer curve from foot to the peak of the band will be less. It is believed that this effect is small enough in our experiments to be ignored. The situation being as described, the only quantity which will determine the magnitude of the microphotometer deflections corresponding to a given band is the number of molecules in the absorption cell at the time of exposure which are capable of absorbing light of the frequency corresponding to the band.

A mathematical justification of equation (1) will now be given.

Let n_A = No. of molecules per cc. in state A (trans form) of o-chlorophenol.

n_B = No. of molecules per cc. in state B (cis form) of o-chlorophenol.

D_A = microphotometer deflection corresponding to the A band

D_B = microphotometer deflection corresponding to the B band.

By assumption:

$$n_A = f_A\left[D_A\right]$$
$$n_B = f_B\left[D_B\right]$$

These expressions mean that for a given series of photographs of the absorption spectrum there is an unchanging functional relationship between the microphotometer deflection and the concentration of molecules which correspond to a given absorption band. This functional relationship depends on the behavior of the photographic plate at the frequency in question, upon the shape and width of the band and upon the transition probability corresponding to the band. Other factors such as the intensity of the light source, illumination of the slit, setting of the microphotometer are held constant. Dependence on the photographic process is eliminated by the use of a single photographic plate for a given series of exposures.

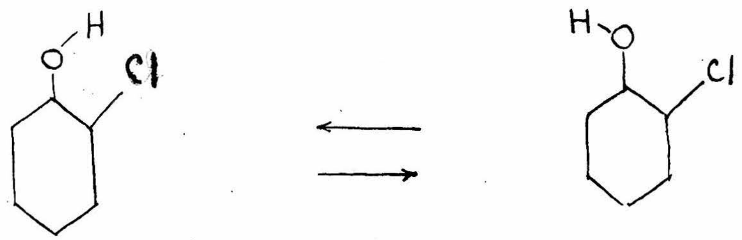
Let P = total pressure of o-chlorophenol vapor. To the approximation that o-chlorophenol vapor obeys the perfect gas laws we have, at the temperature T_1, that:

$$\left.\begin{aligned} n_A &= c_A P \\ n_B &= c_B P \end{aligned}\right| \text{ where } c_A \text{ and } c_B \text{ are constants at the given temperature}$$

Suppose $(D_A)_{T_2,P_2}$ and $(D_B)_{T_2,P_2}$ are the microphotometer deflections for the A and B bands corresponding to an absorption spectrum of the vapor taken at the temperature T_2 and the pressure P_2. Then using the curves obtained from absorption spectra photographed with the vapor temperature was T_1 (see Fig. 4) one finds the pressure P_x at which $(D_A)_{T_1,P_x} = (D_A)_{T_2,P_2}$. Since $n_A = f_A\left[D_A\right]$ then $(n_A)_{T_1,P_x} = (n_A)_{T_2,P_2}$. That is, the number of molecules in the absorption cell in state A when the temperature is T_1 and the pressure is P_x is equal to the number of molecules in state A when the exposure is made at the temperature T_2 and the pressure P_2. The concentration of molecules in the absorption cell in configuration B at temperature T_2 and pressure P_2 is given by $(n_B)_{T_2,P_2} = c_B P_Y$ where P_Y is the pressure corresponding to the value $(D_B)_{T_1} = (D_B)_{T_2,P_2}$ on the D_B-pressure curve (Fig. 4). The concentration of molecules in form B at the temperature T_1 and pressure P_x is given by $(\ _B)_{T_1,P_x} = c_B P_x$

$$\frac{\left(\frac{n_A}{n_B}\right)_{T_2,P_2}}{\left(\frac{n_A}{n_B}\right)_{T_1,P_x}} = \frac{(n_B)_{T_1,P_x}}{(n_B)_{T_2,P_2}} = \frac{c_B P_x}{c_B P_y} = \frac{P_x}{P_y}$$

Let us consider the reaction



o-chlorophenol
cis form
(corresponds to
B band)

o-chlorophenol
trans form
(corresponds to
A band)

Employing the thermodynamic symbols used by Lewis and Randall we can write

$$\Delta V = 0$$

thus it follows that

$$\Delta H^\circ = \Delta E^\circ$$

also

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = 0 \quad \text{where } K = \left(\frac{n_A}{n_B}\right)$$

Furthermore

$$\left(\frac{\partial \ln K}{\partial 1/T}\right)_P = -\frac{\Delta E^\circ}{R}$$

thus

$$\ln \frac{K_{T_2}}{K_{T_1}} = \ln \frac{\left(\frac{n_A}{n_B}\right)_{T_2,P_2}}{\left(\frac{n_A}{n_B}\right)_{T_1,P_x}} = \ln \frac{P_x}{P_y} = \frac{\Delta E^\circ (T_2 - T_1)}{R \quad T_1 T_2}$$

$$\Delta E^\circ = \left(\frac{T_1 T_2}{T_2 - T_1}\right) R \ln \frac{P_x}{P_y} \qquad (1)$$

In the employment of the above described method for the evaluation of ΔE°, there are quite a few places where errors can creep in. The illumination of the slit may not have been quite the same for all exposures, the photographic plate may not have been sensitized or developed quite uniformly or the microphotometer may have shown a slight change of behavior with time. A large uncertainty arises in the measurement of the microphotometer deflection on the microphotometer plates. On account of the irregular nature of the microphotometer curve, due largely to graininess and irregularities of the photographic plate, it is difficult to decide upon the true height of the peak of an absorption curve above the foot of the curve. This is particularly true in the case of the weak A band. The accuracy of measurement of the microphotometer deflection corresponding to the A band is decisive in determining the accuracy of evaluation of ΔE°. The error may be as much as twenty percent.

The difference in the free energies of the two forms of o-chlorophenol may also be evaluated if, for the series of exposures previously described, the functional relationship between the microphotometer deflection and concentration of molecules corresponding to a given band is identical for the A and B band. This ought to be true if the following conditions hold: (1) the behavior of the photographic plate is the same at both band frequencies (2) the shape and width of each band is the same (3) the transition probabilities of both bands are the same. The first condition is fairly well satisfied because Z plates whose sensitivity is practically constant with wavelength in this region, were used. A consideration of the microphotometer curves of the third harmonic O-H band of o-chlorophenol obtained by Badger and Bauer[2] indicates that the second condition holds to a fair approximation. The studies of Wulf and Liddel[7] on the second harmonic O-H bands of o-chlorophenol dissolved in CCl_4 seem to indicate that the transition probabilities for the A and B bands are about equal. If this also holds for the third harmonic bands, then, the third condition is satisfied. It is seen that we have reasons for believing that the functional relationship between the microphotometer deflection and concentration of molecules corresponding to a given band is approximately identical for the A and B bands of o-chlorophenol. In the ideal situation, where the functional relationships are identical, suppose s equals the factor by which the abscissa of the D_A curve must be reduced so that the D_A curve will coincide with the D_B curve (see Fig. 4), then s will equal the ratio of the concentrations of the two molecular species.

Let us consider a mathematical justification of the last statement. Now

$$n_A = f\left[D_A\right] \quad (2)$$
$$n_B = f\left[D_B\right] \quad (3)$$

where f in each equation denotes the same function.

Let

N_A = mole fraction of molecules in the trans form

N_B = mole fraction of molecules in the cis form

P'_A = pressure corresponding to $D_A = D'_A$ on the D_A-pressure curve (Fig. 4)

P'_B = pressure corresponding to $D_B = D'_B$ in the D_B-pressure curve.

Suppose $D'_A = D'_B$, then according to equations (2) and (3)

$$n_A = n_B$$

but according to the perfect gas laws

$$n_A = \frac{P'_A}{kT_1} N_A$$

and

$$n_B = \frac{P'_B}{kT_1} N_B$$

k = Boltzman's constant

T_1 = absolute temperature of vapor when absorption spectra were photographed

thus

$$\frac{P'_A}{P'_B} = \frac{N_B}{N_A} = \left(\frac{n_B}{n_A}\right)_{T_1,P}$$

but

$$s = \frac{P'_A}{P'_B} \qquad \therefore \quad s = \left(\frac{n_B}{n_A}\right)_{T_1,P}$$

Now according to thermodynamics

$$\Delta F^{\circ} = - RT_1 \ln K = - RT_1 \ln \left(\frac{n_A}{n_B}\right)_{T_1,P}$$

but

$$\left(\frac{n_A}{n_B}\right)_{T_1,P} = \frac{1}{s}$$

$$\therefore \qquad \Delta F^{\circ} = RT_1 \ln s \qquad (4)$$

We repeat that s is the factor by which the abscissa of the curve corresponding to the 10,443 cm^{-1} band must be reduced in order that this curve coincides with the curve corresponding to the 10,189 cm^{-1} band (see Figure 4). ΔF° is the difference in standard free energies of the trans and cis forms of o-chlorophenol and R is the gas constant.

Employing equation (4) one can easily calculate ΔF° from the photometric data plotted as in Figure 4. This method of calculating ΔF° involves additional assumptions besides those made in the calculation of ΔE°, but the previously mentioned uncertainty in the values of the microphotometer deflections probably outweighs any of the other uncertainties.

Experimental Results of the Photometric Study of Orthochlorophenol.

Three preliminary photometric experiments I, II and III and two more extensive experiments IV and V were made on o-chlorophenol. The data and experimental results are given in Table II.

An Average of several experiments gives for o-chlorophenol

Table II

Photometric study of orthochlorophenol

D_A (cm.)	D_B (cm.)	T (°K)	P (mm. Hg.)	E° $\left(\frac{\text{kcal}}{\text{mole}}\right)$	F° $\left(\frac{\text{kcal}}{\text{mole}}\right)$
Experiment I					
0.43	3.90	453	255		
0.57	5.70	453	410		
0.70	3.56	542		4.3	
0.96	5.05	543			2.2
Experiment II					
0.73	4.22	459	133		
0.83	5.24	459	192		
0.94	6.16	459	281		
1.37	6.50	539		3.5	2.6
Experiment III					
0.56	4.30	457	146		
0.78	5.39	458	232		
0.89	6.49	458	334		
0.90	5.20	540		2.8	
1.09	5.87	540		3.7	2.6
Experiment IV					
0.40	1.99	460	32.6		
0.43	3.41	460	79.3		
0.61	4.37	461	160		
0.98	6.42	461	301		
1.53		463	638		
0.92	4.53	534		4.3	
0.79	4.29	537		3.6	
0.87	4.50	537		3.8	
					3.0

Table II (continued)

D_A cm.	D_B cm.	T °K	P mm Hg	E° $\frac{\text{kcal}}{\text{mole}}$	F° $\frac{\text{kcal}}{\text{mole}}$
Experiment V					
0.30	1.76	450	36.7		
0.50	3.10	450	78.5		
0.62	4.42	451	166		
0.91	6.39	450	314		
	1.60	451	676		
0.70	3.25	537		4.5	
0.60	2.87	537		4.6	
0.58	3.14	537		3.6	
					2.7

D_A = Microphotometer deflection corresponding to band at 10,443 cm^{-1}

D_B = Microphotometer deflection corresponding to band at 10,189 cm^{-1}

T = Temperature of o-chlorophenol vapor in absorption cell

P = Pressure of o-chlorophenol vapor in absorption cell

ΔE° = 3.5 kcal./mole and ΔF° = 2.8 kcal./mole (at 180°C) where these are energy differences between the cis (chelated) and trans (non-chelated) forms of the molecule. As previously discussed, the accuracy in measurement of D_A is not very great; consequently the uncertainty in the above values may be as much as twenty percent of their given value.

Photometric Study of N-propyl Alcohol and Ethylene Chlorohydrin

It was found in the study of n-propyl alcohol that the change in the ratio of the intensities of the doublet band was within the uncertainties imposed by the nature of the experiment. From this it may be estimated that the upper limit for ΔE° for the two hypothetical configurations[2] is about 0.8 kcal./mole.

Ethylene chlorohydrin was studied in a manner similar to o-chlorophenol. In this case, one must consider three microphotometer deflections D_A, D_B and D_C which correspond respectively to the maxima of the doublet band at 10,546 cm^{-1} and 10,485 cm^{-1} and to the band at 10,367 cm^{-1}. The difference in the energy of the molecular configurations corresponding to the normal doublet band and the configuration corresponding to intramolecular hydrogen bond formation was calculated. The data and results of two photometric experiments on ethylene chlorohydrin are listed in Table III. An average value of ΔE° is 2.0 kcal./mole. This value is subject to an uncertainty of, perhaps, twenty percent.

Table III

Photometric study of ethylene chlorohydrin

D_A cm.	D_B cm.	D_C cm.	T °K	P mm. Hg	E° $\frac{\text{kcal}}{\text{mole}}$
Experiment I					
1.00	1.61	2.87	425	490	
1.22	1.89	3.29	425	646	
2.05	2.96	4.90	425	1048	
1.42	2.22	2.60	531		1.9
Experiment II					
1.00	1.72	2.87	420	417	
1.65	2.40	3.99	421	709	
2.29	3.42	5.12	421	1120	
0.87	1.32	1.70	516		2.1

D_A = Microphotometer deflection corresponding to absorption maximum at 10,546 cm^{-1}

D_B = Microphotometer deflection corresponding to absorption maximum at 10,485 cm^{-1}

D_C = Microphotometer deflection corresponding to absorption maximum at 10,367 cm^{-1}

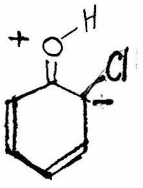
T = Temperature of ethylene chlorohydrin vapor in absorption cell

P = Pressure of the vapor in the absorption cell.

Discussion of the Results of the Temperature Effect Studies

The value of $\Delta E°$ for o-chlorophenol, which corresponds to the energy of the intramolecular hydrogen bond formation, appears to be related to the frequency difference of the two observed bands in the manner which one would expect from the relation between frequency shift and interaction energy pointed out by Badger and Bauer[8]. This relation also seems to apply to case of ethylene chlorohydrin, although $\Delta E°$ in this case involves the difference in the C-Cl and C-O dipole interactions as well as hydrogen bond energy.

It is a little difficult to be certain concerning this point but it appears that the oxygen-chlorine hydrogen bond is stronger in the case of o-chlorophenol than it is in the case of ethylene chlorohydrin. One might expect the hydrogen bond to be stronger in the former case because in o-chlorophenol we have a quantum mechanical resonance which tends to increase the ionic character of the O-H bond. Contribution from the resonance form



should especially enhance the electrostatic interaction between the hydrogen and chlorine atoms.

The value of $\Delta F = 2.8$ kcal/mole (180°C) is to be compared with $\Delta F = 1.4$ kcal/mole calculated by Pauling[1] from the data of Wulf and Liddel[6] on the second harmonic bands of o-chlorophenol dissolved in carbon tetrachloride. Since the O-H in the trans position will have a slight interaction with the solvent molecules one might expect the ΔF° for o-chlorophenol in solution to be a little less than in the vapor, however, the difference in the two values seems a bit large. According to microphotometer curves of Badger and Bauer[2] the A band appears to be a little broader than the B band. This should have the effect of making our estimated value of ΔF° a little high.

The values of $\Delta E^{\circ} = 3.9$ kcal/mole and $\Delta F^{\circ} = 2.8$ kcal. /mole for o-chlorophenol give the entropy difference as 2.4 entropy units. This means that the trans configuration of o-chlorophenol has the higher entropy value. When one considers the plot of the potential energy of the molecule against rotation of the hydroxyl hydrogen around the C-O bond, a shallower and perhaps broader potential minimum compared with the minimum for the cis form seems reasonable for the trans form of the molecule. Applying the ideas of statistical mechanics in a qualitative way, we decide that we would expect a greater entropy to be associated with the trans form of the o-chlorophenol molecule. Furthermore the interaction of the hydroxyl hydrogen with the chlorine atom may increase the C-Cl bending frequency. This would tend to further increase the entropy of the trans form with respect to the cis form.

Summary of Important Points

Points of importance or interest arising from this research.

1. Evidence for intramolecular hydrogen bonds has been found for several substituted alcohols.

References

[1] Pauling, J. A. C. S. 58, 94 (1936)

[2] Badger and Bauer, J. Chem. Phys. 4, 711 (1936)

[3] Barchewitz and Freymann, Compte rendu. 204, 1728 (1937)

[4] Herzberg, Patat and Verleger, J. Phys. Chem. 41, 123-32 (1937)

[5] Wulf, Liddel and Hendricks, J. A. C. S. 58, 2287 (1936)

[6] L. Pauling and L. O. Brockway, Proc. Nat. Acad. Sci., 20, 336 (1934)

[7] Wulf and Liddel, J. A. C. S. 57, 1464 (1935)

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

Summary

Summary of the Main Results of Research

In the paper entitled *The Band Envelopes of Unsymmetrical Rotator Molecules. I. Calculation of the Theoretical Envelopes.* the envelopes of the three elementary types of band have been calculated by an approximation method for nine different sets of molecular parameters. This work constitutes the first calculation of the theoretical envelopes of unsymmetrical molecules. The calculated envelopes are of assistance in interpreting the observed bands of heavy unsymmetrical molecules.

A rotational analysis of the third harmonic O-H band in formaldoxime vapor was made in the publication *An Absorption Band of Formaldoxime at λ 9572.* The information ,thus obtained, regarding the moments of inertia of the molecule when combined with data obtained from electron diffraction measurements will probably be of assistance in locating the position of the hydroxyl hydrogen in the molecule. The appearance of the absorption band indicates that the hydroxyl hydrogen does not rotate freely about the N-O bond.

The *Investigation of the Third Harmonic O-H Band of Substituted Alcohols* gives spectroscopic evidence for intramolecular ~~gives~~ hydrogen bonds in the case of several substituted alcohols. A change with temperature of the relative intensities of the two bands of o-chlorophenol was observed for the first time. The direction of the change is in agreement with the explanation (by Linus Pauling) for these two bands. The photometric study of the effect of temperature on the O-H bands of ethylene chlorohydrin and o-chlorophenol gives the corresponding energies of intramolecular hydrogen bond formation and also the entropy difference of the cis and trans forms of o-chlorophenol.

Propositions

Propositions

1. The assertion[1] that the carboxyl hydrogen nucleus is held less strongly in the halogenated acids of enhanced acid strength than in the non-halogenated acids is incompatible with experimental evidence.

[1] I. Langmuir, Chem. Rev. 6, 465 (1929).

2. Plyler and Williams[1] state that the absorption coefficient for the fundamental band of HCl dissolved in benzene is approximately three or four times greater than the same for HCl in the gaseous state. A slight extension of Fairbrother's[2] treatment indicates that if $(d\mu/dr)_{r_e}$ is negative[3] for gaseous HCl then $(d\mu/dr)_{r_e}$ is positive for HCl in solution.

[1] Phys. Rev. 49, 215 (1936).

[2] Fairbrother, Trans. Faraday Soc. 33, 1507 (1937).

[3] Bartholome, Z. f. physik. Chem. B 33, 131 (1933); Bell and Coop, Trans. Faraday Soc. 34, 1209 (1938).

3. Intramolecular hydrogen bond formation which is indicated by spectroscopic studies of substituted alcohols and phenols is also indicated by a comparison of the heats or entropies of vaporization of these substances with the corresponding quantities for the unsubstituted compounds.

4. A perhaps over-simplified consideration of the effect of the liquid state on vibrational frequencies such as the

O-H valence vibration of alcohols leads one to conclude that $\frac{\nu_{liq} - \nu_{gas}}{\nu_{gas}}$ is in the first order linearly dependent on $\left(\frac{\partial \phi}{\partial r}\right)_{r_e}$ and $\left(\frac{\partial^2 \phi}{\partial r^2}\right)_{r_e}$ where both of these derivatives have positive coefficients. ϕ represents the potential energy of interaction of the molecule of interest with its neighbors and is considered as being expansible in terms of r, the normal coordinate corresponding to the valence vibration. $\Delta \nu / \nu$ will be proportional to the energy of interaction for a special form of ϕ but in general need not be.

5. Taking the Gurney and Mott[1] theory of latent image formation as a working hypothesis it is proposed that in the process of growth of silver specks, during which silver ions in interlattice positions are attracted to the charged silver (on the surface of the grain), the hydrogen ions from the contiguous gelatine will be attracted to the silver speck, become neutralized and interfere with the growth of the speck. Hypersensitization which seems to involve the replacement of hydrogen ions on the gelatine by silver ions[2] would reduce this interfering effect and thus make the emulsion more sensitive.

[1] Gurney and Mott, *Proc. Roy. Soc.* 164 A, 151 (1938).

[2] Carroll and Hubbard, *Bur. Standards J. Res.* 10, 211 (1933).

6. In the calculation of pressure-composition isotherms of

binary mixtures of hydrocarbons such as propane and butane from the data on the pure components where one applies ideal solution laws the best approximation to actual data seems to be obtained when one employs fugacities and fugacity/pressure ratios which are intermediate between those for the substances at the given temperature and pressure and those for the corresponding saturated liquid or gas.

7. Gaseous mixtures even at low densities are not, strictly speaking, ideal solutions. The following equation is proposed for an approximate evaluation of the fugacity (at low densities) of a component of a binary gaseous mixture.

$$\ln \frac{f_1}{f_1^\circ N_1} = 2P \left[\left\{ - \frac{Z_1}{P} \right\}_T^{1/2} + \left\{ - \frac{Z_2}{P} \right\}_T^{1/2} \right]^2 N_2^2$$

f = fugacity of component in mixture

f° = fugacity of pure gas at same temperature and pressure

$Z = PV/RT$

N = mole fraction

8. The Claude Bernard theory revived by Bancroft[1] asserts that the reversible coagulation of protein colloids of the sensory nerves produces or accompanies anesthesia. It is here suggested that the native protein in the nerve cells may only be reversibly denatured with temporary loss of certain specific properties necessary for the functional behavior of these proteins. One notes that almost all direct anesthetics

or narcotics are capable of taking part in hydrogen bond formation thus according to the Mirsky-Pauling[2] picture of denaturation these substances could induce denaturation.

1. Bancroft, J. Phys. Chem. 35, 215 (1931).
2. Mirsky and Pauling, Proc. Nat. Acad. Sci. 22, 439 (1936).

9. There is a great variety of evidence in the literature which indicates that a "hydrogen" bond involving deuterium is stronger than a hydrogen bond involving hydrogen.

10. The case of breaking the carbon-carbon bond when the two adjacent carbon atoms are loaded with negative atoms like chlorine and oxygen, as evidenced by the decomposition of trichloroacetic acid, trichlorophenomalic acid, etc. when these substances are boiled with water, is to be thought of as due to the increased ionic character of the carbon-carbon bond rather than due to a decrease in the strength of this bond.

11. Experimental evidence seems to indicate that the satellite band on the low frequency side of the pyrrole N-H bond arises neither from a situation wherein the effective electric moment of the N-H group is divided between two normal modes of vibration nor from two molecular species of pyrrole[1] but that the satellite is the first member of a sequence of transitions in which in both the upper and lower states, corresponding to the N-H band, a low frequency vibration is excited.

1. L. Pauling, J. A. C. S. 58, 96 (1936).