

A Partial Analysis of Some InfraRed Absorption Spectra of Organic Molecules in Dilute Solution

Oliver R. Wulf and Lola S. Deming

Citation: [The Journal of Chemical Physics](#) **6**, 702 (1938); doi: 10.1063/1.1750154

View online: <http://dx.doi.org/10.1063/1.1750154>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[InfraRed Absorption Spectra at Low Temperatures](#)

J. Chem. Phys. **18**, 552 (1950); 10.1063/1.1747682

[The InfraRed Absorption Spectra of Some Metal Borohydrides](#)

J. Chem. Phys. **17**, 1044 (1949); 10.1063/1.1747110

[InfraRed Absorption Spectra of Organic Compounds](#)

J. Chem. Phys. **17**, 218 (1949); 10.1063/1.1747226

[InfraRed Absorption Spectra of Some Octenes](#)

J. Chem. Phys. **15**, 135 (1947); 10.1063/1.1746443

[The Absorption Spectra of Sugars in the Near InfraRed](#)

J. Chem. Phys. **8**, 51 (1940); 10.1063/1.1750566



Murphy¹³ has given analytical expressions for describing the free energy, entropy and heat capacity as functions of the temperature. The application of these to allene has been discussed by Linnett and Avery,¹⁴ where it was found that the more complicated molecule necessitated the introduction of an extra term into the expressions for $-(F-E_0^0)/T$ and S and that the heat capacity required an even more complicated expression. Expressions similar to those for allene were used for cyclopropane. The equations for the translational and rotational parts of $-(F-E_0^0)/T$ and S are:

$$-(F-E_0^0)/T = 18.300 \log T + 2.112,$$

$$S = 18.300 \log T + 10.060$$

and for the vibrational parts:

$$-\frac{(F-E_0^0)}{T} = 131.60 - \frac{34.757 \log T}{T}$$

$$- 51.386 \log T + 4.395T \times 10^{-2}$$

$$- 0.686T^2 \times 10^{-5} + \frac{36.289 \times 10^2}{T},$$

$$S = 109.28 - 51.386 \log T$$

$$+ 8.791T \times 10^{-2}$$

$$- 2.058T^2 \times 10^{-5} - \frac{15.095 \times 10^2}{T}.$$

The equations for the complete values of

¹³ Murphy, J. Chem. Phys. 5, 637 (1937).

¹⁴ Linnett and Avery, J. Chem. Phys. 6, 686 (1938).

$-(F-E_0^0)/T$ and S are then:

$$-\frac{(F-E_0^0)}{T} = 133.71 - \frac{34.757 \log T}{T}$$

$$- 33.086 \log T + 4.395T \times 10^{-2}$$

$$- 0.686T^2 \times 10^{-5} + \frac{36.289 \times 10^2}{T},$$

$$S = 119.34 - 33.086 \log T$$

$$+ 8.791T \times 10^{-2}$$

$$- 2.058T^2 \times 10^{-5} - \frac{15.095 \times 10^2}{T}.$$

The equations for the vibrational components of $-(F-E_0^0)/T$ and S reproduce the values in Table XII very well between 200 and 1000°K, but not so well between 100 and 200°. Nevertheless the equations for the total values of $-(F-E_0^0)/T$ and S reproduce the tabulated values within 0.2 percent over the whole range between 100° and 1000°.*

I wish to thank Professor E. Bright Wilson, Jr., who suggested my studying these compounds, for his advice during this work.

* Uncertainty in the calculated values of the thermodynamic quantities may arise from several causes. In the first place there is uncertainty in our knowledge of the frequencies both from experimental inexactitude and also because Raman measurements were made on the liquid. Another source of error comes from our lack of knowledge regarding the anharmonicities of vibrations in polyatomic molecules.

A Partial Analysis of Some Infra-Red Absorption Spectra of Organic Molecules in Dilute Solution*

OLIVER R. WULF AND LOLA S. DEMING
Bureau of Chemistry and Soils, Washington, D. C.
(Received August 18, 1938)

An attempt is made to resolve into component parts a number of relatively complex infra-red absorption coefficient curves for several OH-containing organic molecules in the region of the first overtone absorption of the OH group. Such analyses suggest certain relations between the structure of the molecule and its effect upon the character of the absorption of the absorbing group.

IN dilute solution of a nonpolar solvent such as carbon tetrachloride, the absorption in the

near infra-red characteristic of the presence of a single OH or NH group in an organic molecule is often relatively simple, the curve of the absorption coefficient consisting of one or two absorption peaks which are narrow and fre-

* Material presented at the Rochester meeting of the American Chemical Society, September 1937, and at the Indianapolis meeting of the American Association for the Advancement of Science, December 1937.

quently symmetrical. A considerable number of molecular absorption coefficient curves of this type, measured in the region of the first overtone, have been published in articles from this laboratory during the last few years. In the present article an attempt is made to resolve certain of the more complex absorption curves published in the above-mentioned work into simple component peaks and to relate the results to the structure of the absorbing molecules. Insofar as this can be accomplished the work seems to comprise an analysis of the vibrational spectra of such molecules. These infra-red spectra in solution seem to be devoid of structure that would suggest discrete rotational transitions, and appear to consist of material originating in the vibrational motions within the molecule. Frequently a characteristic vibration of a polyatomic molecule is such that appreciable amplitude of vibration occurs only within a single group, as the O—H or C=O group, and such a vibration is often spoken of as an OH vibration or a C=O vibration. This article is principally concerned with absorption spectra characteristic of the presence of the OH group in certain molecules.

The present work is based on the assumption that absorption coefficient curves, such as those mentioned above, are in reality the superposition of a number of single symmetrical peaks, each single group such as OH or NH in one particular position and orientation in the molecule giving rise to one of these peaks. That these component peaks should be symmetrical is not evident *a priori* but will be assumed here. Proceeding on this basis it is possible, in a rather natural way, to resolve several of the absorption coefficient curves in the above-mentioned papers into a small number of component curves. In some cases these analyses lead to suggestions regarding the structure of the absorbing molecules, and it is believed that they may afford an aid in the utilization of this type of spectra by the chemist. Moreover, in those cases where there is now reason for expecting two symmetrical peaks, such as in certain of the *ortho* substituted phenols, this process of decomposing the over-all curve into components seems to be a justifiable procedure.

It is experimentally difficult to measure such absorption coefficients with high accuracy and

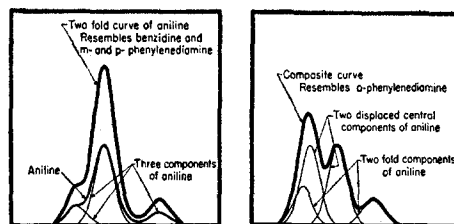


FIG. 1. Possible components of the absorption characteristic of the presence of NH_2 in *m*- and *p*-phenylenediamine and benzidine, and in *o*-phenylenediamine, using aniline as a basis.

in what follows the expression "symmetrical peak" is used to differentiate those peaks which appear single and at least nearly symmetrical from those which are evidently asymmetrical or which contain more than one actual maximum. There may, however, be present in what may at a cursory glance appear as a single symmetrical peak, a small amount of real asymmetry but which may lie within the rather wide limits of experimental error to which such quantitative measurements are often subject. In this paper the attempt will be made to discuss the structure of some absorption coefficient curves which are evidently complex in terms of certain of the more typical single peaks which are at least practically symmetrical. It seems necessary to neglect slight deviations from exact symmetry in the experimental results from whichever cause they may have arisen, in order to progress in the work of analyzing the more complicated curves.

Before discussing those cases in which a rather careful analysis has been attempted, it may be helpful to give a somewhat rough illustration of the reasonableness of breaking up complex curves in this way. Such an illustration is contained in the curves for the amino analogs of catechol, resorcinol, and hydroquinone, the curves for the latter group affording a relatively simple basis of reference.¹ The curves for *m*- and *p*-phenylenediamine, and indeed also for the substance benzidine, resemble the curve for aniline, whereas a considerable change occurs in passing to *o*-phenylenediamine.² To see the

¹ Wulf and Liddel, J. Am. Chem. Soc. **57**, 1464 (1935).

² In the discussion in reference 1 these cases were mentioned, pointing out that reference to the OH analogs indicated that it should be possible to resolve the curves for these amino compounds into component peaks, and that a certain parallelism existed between the behavior of the two sets of compounds.

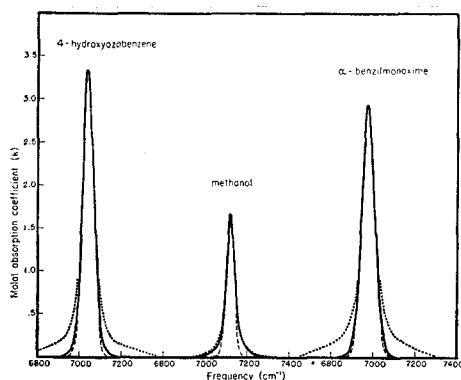


FIG. 2. A comparison of the form $(\cdots) y = \frac{y_0}{1 + (x^2/a^2)}$ and the form $(---) y = y_0 e^{-a^2 x^2}$ with experimental curves.

nature of this change, it is necessary to consider the character of the curve for aniline.¹

The absorption characteristic of the NH_2 group in aniline in the region 6000–7000 cm^{-1} may be approximately resolved into three symmetrical component peaks, as indicated in Fig. 1. The two principal components are at roughly 6680 and 6880 cm^{-1} , respectively. These two peaks, while varying in intensity and also somewhat in separation from compound to compound, seem to characterize the presence of an NH_2 group. This suggests that they may represent two modes of vibration of the group which in analogy to water might be somewhat loosely termed the parallel valence vibration and the asymmetrical vibration. The third peak at roughly 6580 cm^{-1} differs considerably when the group appears in different molecules, giving indication that it arises from interaction with the rest of the molecule which varies with the structure. In certain molecules containing the NH_2 group, still further detail can be seen, indicating a more complicated interaction with the remainder of the molecule. Using this structure of the absorption of aniline, one may make the absorption curves for the three phenylenediamines and benzidine somewhat clearer by the process of resolution just described. The curves for *m*- and *p*-phenylenediamine and for benzidine, while differing somewhat from one another, may be approximately represented by a curve derived from the aniline curve itself multiplied by a factor of two, as shown in Fig. 1. This is not surprising when one recalls that the

only striking difference between hydroquinone and resorcinol on the one hand and phenol on the other was the twofold greater intensity of the absorption of the former two, indicating that the two OH groups were practically independent of one another, that is, simply additive. In the case of catechol, however, two separate phenol-like peaks were found, the separation in this instance being about 100 cm^{-1} . Turning now to the absorption curve for *o*-phenylenediamine, which appears more complicated than those of the other three, it may be approximated, as shown in Fig. 1, by the simple addition of both the second and third peaks of aniline multiplied by a factor of two, and two peaks of the first frequency of aniline separated from one another by a spacing which happens here also to be about 100 cm^{-1} . This analysis of the *o*-phenylenediamine curve, which is suggested by the relatively simple result for catechol, affords an illustration of the basis for attempting to break up complex curves in this way.³

In the above, the only condition placed on the component curves was that they be symmetrical, their shapes being determined by choosing symmetrical curves which would best fit the complete observed curve. In proceeding now to discuss some observed curves which have been resolved with more care, the question of the shape of the individual peaks, postulated as characterizing any single OH or NH group in a particular position and orientation, becomes of importance. These curves are frequently surprisingly sharp as was discussed in reference 1. For the theory of their breadths, it is, of course, of particular interest to know whether the shape of such curves may be represented by any simple analytical expression. Two relatively simple forms suggest themselves as possibilities: (1) the curve for a damped oscillator, and (2) the Gauss error curve, both of these having at least a possible connection with the actual physical phenomenon. Inspection shows that there is considerable variation among the many measured curves. Some conform more nearly to the one type of curve and some more nearly to the other. In Fig. 2 three curves have been chosen

³ In this connection see for example, Fox and Martin, *Proc. Roy. Soc.* **A162**, 422 (1937); and Rose, *Nat. Bur. Stand. J. Research* **20**, 129 (1938).

to illustrate this, showing, with the experimental curves which were measured in earlier work,⁴ Gauss error and damped oscillator curves in dashed and dotted lines, respectively. The two types of curves have in each case been determined from the value of the ordinate at the maximum and the half-value width of the experimental curves. As can be seen, none of the three conforms closely to either type. However, α -benzilmonoxime and 4-hydroxyazobenzene approximate more nearly the Gauss curve, while methanol, flaring more broadly at the base, approximates more nearly the damped oscillator curve.⁵

In proceeding to break up the more complex curves into their component parts, somewhat less freedom in fitting and hence somewhat more significance in the result is had if one constant form of curve is adopted, this being a reasonable procedure if the breadth of the curve derives from one principal cause. Actually, with an expression which is the sum of the damped oscillator and Gauss error forms of the same half-value widths but with arbitrary values of the ordinates, a very close fit can be obtained with some of the experimental curves, as is perhaps to be expected from Fig. 2. However, it seems probable that the much greater freedom introduced by this procedure should make it possible to fit most symmetrical curves of this type within the limits of error of such experimental measurements and that to do this would sacrifice some of the significance of such analyses. In the work which follows the Gauss error form has been used, and component curves have been placed by trial, attempting in the final addition of the components to obtain as good a representation of the experimental curve as possible. In none of the cases is the representation exact, but in several it is sufficiently close to indicate that the actual curve is to be considered as made up of components at least similar to those employed.

⁴ Hilbert, Wulf, Hendricks, and Liddel, J. Am. Chem. Soc. **58**, 548 (1936); Hendricks, Wulf, Hilbert, and Liddel, *ibid.* **58**, 1991 (1936); and reference 1.

⁵ In the work which follows the Gauss curve will be used. Fig. 2 illustrates a characteristic tendency of the measured curves to persist more strongly in intensity at greater distances from the maximum than does the Gauss curve of the same height and half-value width.

In certain of the *ortho* substituted phenols two distinct peaks characterize the absorption of the OH group, despite the fact that there is only one OH group present. Pauling has suggested⁶ an explanation for this, with which experimental results have proved to be in remarkable accord. The explanation attributes the two peaks to two forms of the molecule, isomers, in which the *orientation* of the OH group differs. It seems probable, as discussed by Pauling, that this is a rather general phenomenon, not restricted to the *ortho* substituted phenols. Certain of the latter, however, offer particularly clear illustrations of this composite form of complex absorption curves.

The absorption of tetrabromocatechol⁷ seems evidently to be composed of at least two peaks. This curve may be fairly well represented by two Gauss curves of forms chosen with reference to the *cis* peak of *o*-bromophenol and the *cis* peak of catechol, since it is reasonable to suppose in a first approximation that if the complete curve is the sum of two components, the two curves just mentioned should indicate their form. This representation of the tetrabromocatechol curve is shown in Fig. 3, the two components being of the same half-value width, which is equal to the *cis* peak of catechol and slightly greater than the

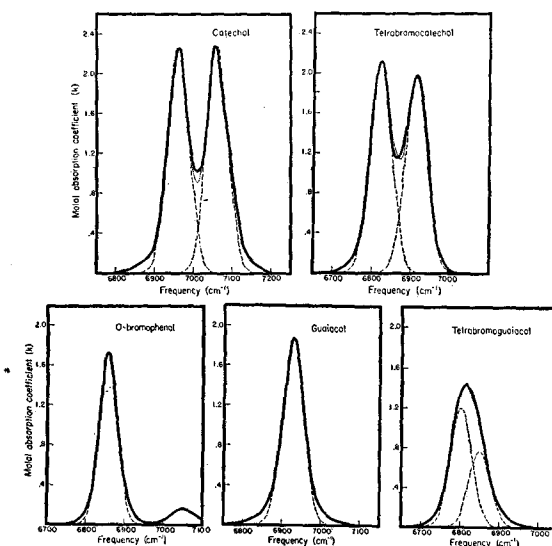


FIG. 3. Resolution of curves for tetrabromocatechol and tetrabromoguaiacol.

⁶ J. Am. Chem. Soc. **58**, 94 (1936).

⁷ Wulf, Liddel, and Hendricks, J. Am. Chem. Soc. **58**, 2287 (1936).

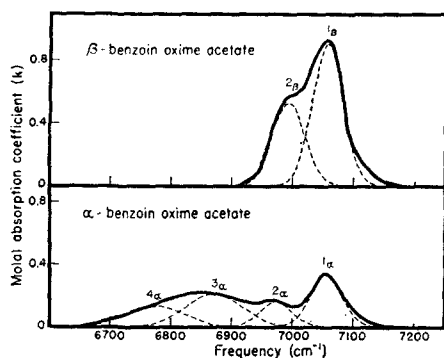


FIG. 4.

cis peak of *o*-bromophenol. The shifted position of a peak relative to the normal phenol position and the increase in the half-value width relative to that of phenol seem to depend on disturbing influences such as nearby polar or polarizable groups in the molecule. There is evidence in the experimental results that an increase in breadth is apt to accompany marked shift in the position of the peak. There are, however, cases where a greater broadening of a peak appears than would be expected from the apparent shift in position of that peak from its normal undisturbed position.

The curve for tetrabromoguaiacol⁷ might be expected similarly to be composed of two peaks, though this is less evident on simple inspection of the curve. However, as was done in tetrabromocatechol, the absorption for tetrabromoguaiacol may be resolved into two components, using the peak for guaiacol and the *cis* peak of *o*-bromophenol as indicating approximately the character of the two component parts. This is shown also in Fig. 3. The half-value widths of the two Gauss curves used are the same, and slightly greater than either that for guaiacol or for the *cis* peak of *o*-bromophenol.

Such resolution of absorption curves into their component parts seems to take on particular significance when applied to certain ordinary geometric isomeric molecular forms. The benzoin oxime acetates illustrate this. By virtue of the

$\text{C}=\text{N}-$ group, benzoin oxime acetate exists

in two isomeric forms similar to fumaric and maleic acids. In the β -form absorption is observed as shown in the upper portion of Fig. 4. That it consists of at least two peaks seems evident,

and the figure illustrates the attempt to fit the observed absorption with two symmetrical curves of the Gauss form and of appropriate intensities and half-value widths. The resulting fit is good except at the right-hand end, this divergence illustrating the tendency mentioned in footnote 5. The curve for the α -form is of particular interest in that it appears to contain in part absorption such as is found in the β -form, reduced in intensity, however, because a portion of the molecules have taken up two other forms indicated by the two curves at the left, which from the point of view of the present work, arise from two new orientations which the OH group may assume in the molecule. These results at first sight might seem to raise the question as to whether the α -form is indeed a pure compound. Dr. A. H. Blatt, who very kindly supplied these compounds originally for measurement, informs us that the behavior of the two materials in characteristic reactions of hydrolysis and cleavage precludes the possibility that there is an appreciable amount of either substance as impurity in the other. We believe the situation should be described by saying that in the α -form, which differs from the β -form fundamentally because of the different orientation with respect to the carbon-nitrogen double bond, the OH group finds four positions, all of which are populated to an appreciable extent and two of which are practically identical with the two positions which the OH group may occupy in the β -form. Benzoin, the parent substance, seems to contain in its absorption¹ principally the two low frequency peaks of the α -form, and suggests that in this molecule the two additional positions of the OH group characterizing the β -oxime acetate and present also in the α -oxime acetate, are absent or but slightly populated.

The isomers of which the two common isomeric forms of benzoin oxime acetate are themselves composed, just as the isomers in *o*-chlorophenol, would seem to be of a rather subtle sort and such perhaps as to defy separation and isolation. However, in the results obtained for another compound which has been studied,⁸ β -2,3,4,6-tetraacetyl-*D*-glucose, there is indication that such forms may yet prove separable. Certain

⁸ Hendricks, Wulf, and Liddel, J. Am. Chem. Soc. **58**, 1997 (1936).

physical properties of the compound showed variations depending on the method of preparation and subsequent treatment. The results of the measurements of the infra-red absorption of this compound indicated similar behavior, the absorption undergoing change concomitant with the change in physical properties such as melting point and optical activity. At room temperature the change was very slow. A high temperature coefficient, however, permitted observing the change in a time of the order of hours in CCl_4 solution at 60°C . After the change was complete, or nearly so, the substance could be returned to its original form by crystallization from ether. A decided alteration in the infra-red OH absorption accompanied this change, the absorption reverting to that which the substance possessed at or near the beginning of the reaction. This OH absorption shows a similarity to that of the benzoin oxime acetates, and it may be represented as composed of nearly the same type of component curves as those of the benzoin oxime acetates. The absorption of two other related compounds, β -2,3,4,6-tetraacetyl-*D*-galactose and α -2,3,4-triacetyl-*D*-xylose, were measured in the same work⁸ and their curves afford additional information concerning the character of the OH absorption in this type of molecule. In Fig. 5 an analysis has been made of the absorption curves for the high and low melting forms of the glucose compound as well as of the curves for the galactose and xylose compounds. The similarity between these absorptions and those of the benzoin oxime acetates can be seen by referring to Fig. 4 and it suggests certain structural features in commons. Past experience has shown that difference in the character of a molecule more than one or two atoms removed from the absorbing group is usually without much effect on the absorption of the group, except in cases where, through the structure of the molecule, an atom several removed in valence bonding has been brought into close proximity to the absorbing group.

The hypothesis of component symmetrical peaks requires that an absorption curve such as that for the high melting form of the glucose compound be composed of at least three peaks, and it seems probable, working by construction from the maximum peak to lower frequencies,

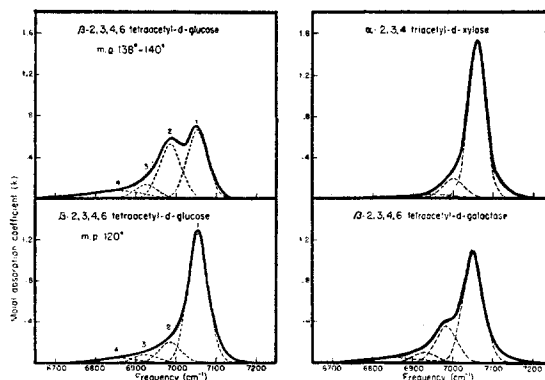


FIG. 5.

that four component peaks describe the absorption better. Thus it seems that in these molecules, also, there exist isomers of the kind composing the two isomeric forms of benzoin oxime acetate. In the spontaneous intramolecular change in which the melting point of the substance falls, the peak at approximately 7050 cm^{-1} increases at the expense of the other three. Thus the relative amounts of the several isomers undergo a change. This change occurs at a rate which increases with temperature, indicating that a potential maximum must be surmounted in each case in the transformation. The fractional change in the peak at about 6890 cm^{-1} is particularly marked.

Thus in β -2,3,4,6-tetraacetyl-*D*-glucose, owing to the slowness of the intramolecular change, what was essentially a partial separation of several forms was possible. This seems to argue for the reality of the picture implied in our primary assumption that an absorption curve such as that of this substance is not a complex absorption of many peaks due to one molecular form (there is, of course, only one OH group in the molecule), but rather is a composite of several simple peaks due to several molecular forms.

It is of particular interest that the spontaneous, that is the thermal, change which β -2,3,4,6-tetraacetyl-*D*-glucose undergoes leads to an increase in the normal OH peak (7050 cm^{-1}) at the expense (diminution) of the three shifted peaks. In accordance with the above interpretation, the shifted peaks should be due to forms of the molecule in which polar groups exist in positions such that the OH group lies in the

vicinity of one of these polar groups. Where an intramolecular change occurs spontaneously, one might expect that this would occur with a decrease in polarity brought about by the change in the orientations of polar groups in such a way as to mutually saturate one another. In accord with this the spontaneous change in the glucose compound is accompanied with a decrease in the melting point, as would be expected in passing from a more polar to a less polar compound. It is of interest in this connection to recall that the preparation of the more polar form (high melting form) of the molecule was effected at will by recrystallization of the compound from the polar solvent ether. Where a solute molecule possesses two or more isomeric forms which differ in polarity and which have but a slight difference in energy, one would expect the polar form to predominate in solution of a polar solvent, while the nonpolar form should predominate in a nonpolar solvent. In the process of crystallization from the polar solvent, the solvent molecules would, so to speak, control the crystallizing out process, putting molecules of the polar form into the growing crystal. For the nonpolar solvent, the reverse would be expected.

Resolution of complex absorption coefficient curves, such as has been illustrated above, could undoubtedly be carried out more successfully were the true form of the component peaks known. This, together with the fact that remarkable sharpness often characterizes single absorption maxima of this kind, makes it particularly desirable to formulate an explanation for the basic cause of the breadth of these absorptions. Important evidence relative to this is contained in the experimental results for the fundamental and first overtone of phenol in CCl_4 solution. Fox and Martin have measured the fundamental, which is shown in Fig. 2 of their article.⁹ The concentration employed was sufficiently high that the association band shows prominently, but the half-value width of the normal OH peak can be seen to be about 25 cm^{-1} . In the work of reference 1, phenol was measured in the first overtone, and as can be seen in Fig. 2 of that article, the half-value width is about 50 cm^{-1} . This twofold increase seems to eliminate any

cause of broadening which would act upon the two absorptions in the same way, such as collision broadening, and strongly suggests that the curves represent the absorption of a distribution of oscillators, in which the restoring force governing the vibration varies slightly about a mean value and in a roughly symmetrical manner, indeed in a manner bearing at least some resemblance to the distribution given by the Gauss curve for errors about the mean value. Each of the oscillators in the distribution behaves independently and produces its own fundamental and first overtone, leading thus to an increase in the breadth of the first overtone by a factor of two. On this hypothesis a cause should be sought which leads to such a symmetrical distribution of all the oscillators around a most probable value.

From the above it seems probable that, even in the cases of complex absorption curves, a single absorption peak characterizes a single OH group in a particular position *and orientation* in the molecule. There is indication that the same thing is true of single NH and CH groups. Where a single peak can be adequately studied, such as the absorption of the OH group in phenol, there seems to be, in sufficiently dilute solution, little or no indication of absorption to either side of the main peak that could be interpreted as the envelope of rotational absorption. Such absorption might be expected if the group were free to rotate, as around the O—C bond connecting the OH group to the ring in phenol. It may be worth while recalling here that the separation of the two rotational maxima for a free OH rotator would be about 150 cm^{-1} , a quantity much larger than the apparent half-value width of a peak such as phenol. As has furthermore been pointed out above, there seems to be good reason to believe that, in many if not most cases, single groups such as OH are constrained to remain in the close vicinity of a preferred position.⁶ An explanation for the observation that single peaks characterize the absorption of single groups under such circumstances has been suggested to the authors by Professor E. Teller. The explanation is similar to that offered by West and Edwards¹⁰ in their work on the absorption of hydrogen chloride in

⁹ Proc. Roy. Soc. **A162**, 419 (1937).

¹⁰ J. Chem. Phys. **5**, 14 (1937).

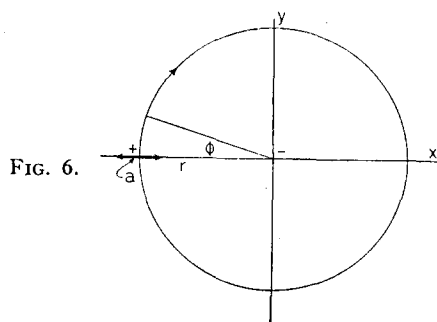


FIG. 6.

solution, in which it is suggested that the observed absorption in this instance is to be described as a principal absorption characterizing the intramolecular vibration together with a nearby subsidiary absorption representing the combination frequency of this high frequency intramolecular vibration with a low frequency intermolecular vibration occurring between the solute and solvent molecules.

If the OH group in phenol is constrained to lie in the plane of the ring, it presumably may librate with small amplitude about its equilibrium position. The restoring force is, of course, not yet known in this instance, but it is presumably sufficiently great to insure that the amplitude will not be large. This relatively low frequency of libration may in general be expected to combine with the principal vibration of the OH group along the valence bond, leading to subsidiary peaks on both sides of the principal frequency displaced by an amount depending on the magnitude of the force constraining the OH group to lie in the plane of the ring. The intensities of the sum and difference frequencies will, of course, differ, the intensity of the peak corresponding to the difference frequency being appreciable only if the restraining force is sufficiently small that the energy of the first quantum in the libration frequency is not too large compared to kT .

Since this factor of the restricted rotational motion of the absorbing group is of importance in discussing the shape of such OH absorptions as that in phenol, it seems worth while to describe here the difference between the absorption of a free dipole rotator and the absorption of such a restricted dipole rotator as we have been considering. In such cases classical theory gives a good approximation for the intensities. The

result for a simple dipole rotator such as a free OH group is well known, but the expressions will be given in order that comparison can be made between these and the expressions for the restricted rotator. In Fig. 6 it can be seen that in the rotational motion of the dipole (drawn for simplicity in this case as if the dipole rotates around a very heavy or fixed center), the variation of the projection of the electric moment on the x axis will be identical to that on the y axis, except for a difference in phase of 90° . If the rotational frequency is designated as ω_r (i.e., $\phi = \omega_r t$) and the vibrational frequency as ω_v (i.e., $s = a \cos \omega_v t$), it is clear that the projection of the electric moment on the x axis may be written approximately as

$$M_x = (M_0 + s(dM/dr) + \dots) \cos \omega_r t \\ = r_0 e \cos \omega_r t + a e' \cos \omega_v t \cos \omega_r t, \quad (1a)$$

$$= r_0 e \cos \omega_r t + (a e' / 2) [\cos (\omega_v + \omega_r) t \\ + \cos (\omega_v - \omega_r) t]. \quad (1b)$$

Expression (1b) consists of three terms, each of which varies periodically. The first possesses the pure rotation frequency, the second possesses the sum of the vibration and rotation frequencies, while the third possesses the difference of the vibration and rotation frequencies. The electric moment associated with the first term $r_0 e$ is larger than that associated with the second and third terms $a e' / 2$, but the first term has a lower frequency than the second and third and the intensities of the three may thus be at least comparable. Simple dipole molecules such as HCl illustrate such behavior.

Considering now the case of a restricted rotator, the angle ϕ instead of passing periodically through 2π is restricted to a libration of relatively low frequency ω_l and of small amplitude γ such that

$$\phi = \gamma \sin \omega_l t \text{ where } \gamma \ll \pi/2 \text{ and hence } \phi \leq \gamma \ll \pi/2.$$

In this case the projections on the x and y axes are different. Introducing the approximations $\sin \phi = \phi$, $\cos \phi = 1$ and referring to (1a) above, the expression for M_x may be written

$$M_x = r_0 e + a e' \cos \omega_v t. \quad (2)$$

Thus M_x varies periodically with the pure vibration frequency and with an amplitude $a e'$,

which is twice as great as the amplitude associated with the sum and difference frequencies in the case of the free rotator. Referring again to (1a) above, the expression for M_y becomes

$$M_y = r_0 e \gamma \sin \omega_l t + (ae' \gamma / 2) [\sin (\omega_v + \omega_l) t + \sin (\omega_v - \omega_l) t]. \quad (3)$$

Expression (3) consists again of three terms, the first representing the pure libration frequency. The amplitude of this is, however, γ times smaller than the pure rotation frequency in the case of the free rotator, although the frequency is indeed slightly higher. The second and third terms are again the sum and difference respectively of the vibration and libration frequencies, but the amplitudes are γ times as small as the amplitude in the case of the free rotator. Since the intensities of emission or absorption are proportional to the square of these amplitudes, the sum and difference frequencies will evidently be very weak relative to the fundamental vibration frequency, if γ is small compared to $\pi/2$.

Thus if the OH group is constrained to lie in a preferred position in the molecule by forces which are sufficiently strong to insure that the amplitude of libration about this preferred position is small at ordinary temperature, the single peaks of absorption characteristically observed for these molecules in dilute solution would find a simple explanation. It seems evident without going through the derivation that, as the amplitude of motion about the preferred position increases, the intensity of the combination frequencies would increase relative to the intensity of the principal frequency. In this suggested explanation for the characteristic single peaks no remark has been made regarding the breadth of these peaks, and it seems necessary to look for some influence on the absorbing group either of an intramolecular or intermolecular nature which would lead to a roughly symmetrical distribution of the groups about a mean as mentioned earlier. This search is perhaps rendered a little more difficult than it would otherwise be by the need of having the distribution symmetrical. It is well therefore to emphasize that the observations indicate only a rough tendency toward symmetry and that an explanation of the breadth of the peaks, which would

lead to asymmetrical broadening of such a nature as to develop pronounced asymmetry only at considerable distances from the maximum, would certainly be admissible.

SUMMARY

Analyses have been made of a number of relatively complex infra-red absorption coefficient curves of certain OH-containing organic molecules in the region of the first overtone absorption of the OH group. The analyses have been based on the hypothesis that such complex curves are in reality the superposition of a number of single symmetrical peaks of varying intensities and positions, each one characteristic of a particular position and orientation of the OH group in the molecule. Relatively simple cases are given in which such resolution into component parts has seemed to be plausible from a consideration of the absorptions of simpler related molecules. In the more complicated cases such analyses appear to afford some information relative to the structure of the absorbing molecule. This has been illustrated in the two isomeric benzoin oxime acetates. In β -benzoin oxime acetate the OH group appears to have two orientations which it occupies to an appreciable extent. In the α -form of this substance four different orientations of the OH group appear, two of which are practically the same as the two orientations in the β -form. In the substance β -2,3,4,6-tetraacetyl-*D*-glucose there are also several orientations which the OH group may take up, presumably four in number, and these resemble those in α -benzoin oxime acetate. The variability in the properties of the β -2,3,4,6-tetraacetyl-*D*-glucose, depending on the method of preparation of the substance, is interpreted as arising from different mixtures of molecules with the OH group in the several orientations. The change with time which the properties of this substance undergo thermally is explained as a change in the relative numbers of molecules possessing the OH group in these several different orientations, and it is suggested that the spontaneous change appears to proceed in the direction in which unsaturated polarity, existing in the molecule and affecting the OH group, is saturated in the change. The observation that

the higher melting form could be obtained by recrystallization from a polar solvent, ether, would seem to be in accord with this. The origin of the single absorption peaks and their relative sharpness is discussed. An explanation for the former, that is, for the observation of what seems to be simply the pure vibration frequency

of the group giving rise to the absorption is suggested, considering the absorbing group as constrained to lie in one or more particular orientations in the molecule by forces which prevent the group departing from such orientations by more than an amplitude small compared with that of rotation around the C—O bond.

NOVEMBER, 1938

JOURNAL OF CHEMICAL PHYSICS

VOLUME 6

The Band Envelopes of Unsymmetrical Rotator Molecules.

I. Calculation of the Theoretical Envelopes *

RICHARD M. BADGER AND LLOYD R. ZUMWALT

*Gates and Crellin Laboratories of Chemistry, California Institute of Technology,
Pasadena, California*

(Received June 14, 1938)

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 Dennison¹ 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 Dennison² and Nielsen³ 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

* 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).