

## The Infrared Absorption of the OH Group of Phenol

Walter Gordy and Alvin H. Nielsen

Citation: [The Journal of Chemical Physics](#) **6**, 12 (1938); doi: 10.1063/1.1750116

View online: <http://dx.doi.org/10.1063/1.1750116>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/1?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Theoretical studies of geometric structures of phenolwater clusters and their infrared absorption spectra in the O–H stretching region](#)

J. Chem. Phys. **105**, 420 (1996); 10.1063/1.471918

[Infrared absorbance spectra and interactions involving OH groups in fused silica](#)

J. Chem. Phys. **69**, 493 (1978); 10.1063/1.436379

[Nature of the Hydrogen Bond. II. The Effect of Hydrogen Bonding and Other SoluteSolvent Interactions upon the Shape and Intensity of the Infrared OH Band of Phenol](#)

J. Chem. Phys. **23**, 2130 (1955); 10.1063/1.1740682

[Combination Frequencies Associated with the First and Second Overtone and Fundamental OH Absorption in Phenol and Its Halogen Derivatives](#)

J. Chem. Phys. **8**, 753 (1940); 10.1063/1.1750576

[The InfraRed Absorption of Phenol and Its Halogen Derivatives in the Region of the Second Overtone of the OH Absorption](#)

J. Chem. Phys. **8**, 745 (1940); 10.1063/1.1750575

---



## The Infrared Absorption of the OH Group of Phenol

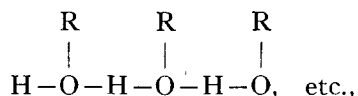
WALTER GORDY\* AND ALVIN H. NIELSEN†

*Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio*

(Received November 1, 1937)

The fundamental vibrational band of the OH group of phenol appearing in the region of  $3\mu$  has been studied for solutions of different concentrations of phenol in benzene, bromobenzene, nitrobenzene, dioxane, and ethyl acetate. The band appears at the same position,  $2.96\mu$ , for the concentrated solutions in all the solvents. In dilute solution in benzene and bromobenzene it appears at  $2.79\mu$ . The band at  $2.79\mu$  is attributed to the OH of single molecules, while that appearing at  $2.96\mu$  in the more concentrated solutions is thought to be due to associated OH. In dilute solutions in the oxygenated solvents the band appears at wavelengths longer than  $2.79\mu$  and is more intense than for the corresponding solution in benzene or bromobenzene. These results are regarded as evidence that the oxygenated solvents form weak additive compounds with the phenol by sharing the proton of the OH group.

IT has been suggested by other writers<sup>1</sup> that phenol in concentrated solutions in solvents such as benzene is probably associated through the formation of hydrogen bonds. It is thought that the phenols as well as the alcohols<sup>1</sup> and water form associated chains:



the oxygen of the hydroxyl group acting as donor and the hydrogen of this group acting as acceptor. Sidgwick suggests that this chain is not likely to contain more than three or four molecules. In extremely dilute solutions molecular weight measurements indicate that the chains are broken and that single molecules predominate. This view has been amply confirmed by infrared measurements for carbon tetrachloride solutions of the alcohols.<sup>2</sup> In these experiments the band which was attributed to the OH group of single molecules appeared at a shorter wave-length by about  $0.25\mu$  than that which was attributed to the associated OH group. Also, the absorption coefficient of the fundamental was less for the single molecules than for

the associated ones. Fox and Martin<sup>2</sup> have reported similar evidence for the association of phenol in carbon tetrachloride solution. Spectroscopic data<sup>3</sup> has been reported favoring the association of water, with a difference of about  $0.3\mu$  in the position of the associated from that of the monomolecular band. In oxygenated or other solvents which contain a donor and can unite with the solute through the formation of hydrogen bonds, observations<sup>4</sup> show that a shift of the OH band of alcohol and of water occurs at rather high concentrations, although in dilute solution in these solvents the band appears at wave-lengths longer by about  $0.10\mu$  than the monomolecular band in dilute solution in carbon tetrachloride. Furthermore the band is more intense when the solvent contains a donor. These results have been advanced as evidence that the solute forms weak hydrogen bonds with solvents of this type.

Infrared evidence has been reported for the existence of intramolecular hydrogen bonds in some of the substituted phenols.<sup>5</sup> Certain *ortho* substituted atoms or groups, particularly C=O, affect appreciably the absorption of the phenolic OH: for example, the absorption curve of o-chloro-phenol shows two distinct peaks in the region  $6500\text{ cm}^{-1}$  to  $7200\text{ cm}^{-1}$ , one near that of

\* Associate Professor of Physics, Mary Hardin-Baylor College, Belton, Texas.

† Assistant Professor of Physics, University of Tennessee, Knoxville, Tennessee.

<sup>1</sup> E. N. Lassettre, *Chem. Rev.* **20**, 259 (1937); N. V. Sidgwick, *The Electronic Theory of Valency* (Oxford University Press, 1929), pp. 134, 149.

<sup>2</sup> J. Errera and P. Mollet, *Comptes rendus* **204**, 259 (1937); J. J. Fox and A. E. Martin, *Nature* **139**, 507 (1937); E. L. Kinsey and J. W. Ellis, *J. Chem. Phys.* **5**, 399 (1937); A. M. Buswell, V. Deitz, and W. H. Rodebush, *J. Chem. Phys.* **5**, 501 (1937).

<sup>3</sup> E. L. Kinsey and J. W. Ellis, *Phys. Rev.* **51**, 1074 (1937); G. B. Bosschieter and J. Errera, *J. de phys. et rad.* **8**, 229 (1937).

<sup>4</sup> W. Gordy, *Phys. Rev.* **51**, 564 (1937); *J. Chem. Phys.* **4**, 769 (1936); *J. Chem. Phys.* **5**, 202 (1937); D. Williams and W. Gordy, *J. Am. Chem. Soc.* **59**, 817 (1937).

<sup>5</sup> O. R. Wulf, U. Liddel, and S. B. Hendricks, *J. Am. Chem. Soc.* **58**, 2287 (1936).

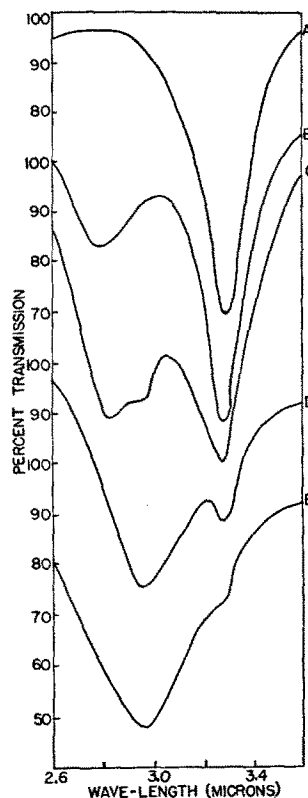


Fig. 1. Percentage transmission of phenol in benzene: A, pure benzene, cell thickness 0.007 cm; B, phenol 0.23 mole/lit., cell thickness 0.007 cm; C, phenol 0.95 mole/lit., cell thickness 0.003 cm; D, phenol 5 mole/lit., cell thickness 0.001 cm; E, phenol 8 mole/lit., cell thickness 0.001 cm.

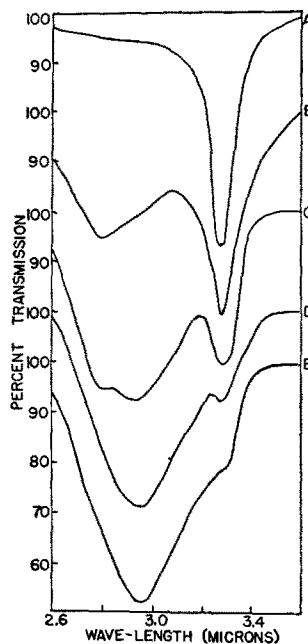


Fig. 2. Percentage transmission of phenol in bromobenzene: A, pure bromobenzene, cell thickness 0.007 cm; B, phenol 0.34 mole/lit., cell thickness 0.007 cm; C, phenol 1.4 mole/lit., cell thickness 0.003 cm; D, phenol 6 mole/lit., cell thickness 0.001 cm; E, phenol 9 mole/lit., cell thickness 0.001 cm.

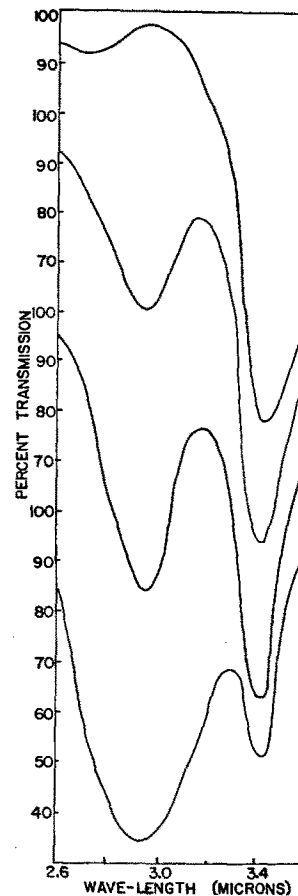


Fig. 3. Percentage transmission of phenol in dioxane: A, pure dioxane, cell thickness 0.007 cm; B, phenol 0.23 mole/lit., cell thickness 0.007 cm; C, phenol 0.95 mole/lit., cell thickness 0.003 cm; D, phenol 8 mole/lit., cell thickness 0.001 cm.

the single peak which occurs in the curve for phenol itself and one at slightly longer wavelengths. In some cases of *ortho* substitution the harmonic of the phenolic OH is absent entirely, and its absence has been taken as a criterion for the presence of strong hydrogen bonds.

Mention has been made of the likelihood of the association of phenol through hydrogen bonding. Huggins<sup>6</sup> has cited evidence for the existence of weak additive compounds between phenols and ketones and between phenols and cyclic ethers which he attributes to hydrogen bridges.

<sup>6</sup> M. L. Huggins, J. Organic Chem. 1, 407 (1936).

It was the purpose of the present study to investigate through measurements of absorption spectra the possibility of the formation of intermolecular hydrogen bonds between phenol molecules, also between phenol molecules and those of certain oxygenated substances. The method used was essentially the same as that used for the study of alcohols.<sup>2,4</sup> Observations were made upon the fundamental vibrational band of the OH group for different concentrations of phenol in the several solvents.

A 60° rocksalt prism of 7 cm face was used. To increase the dispersion of the instrument the light was caused to pass through the prism

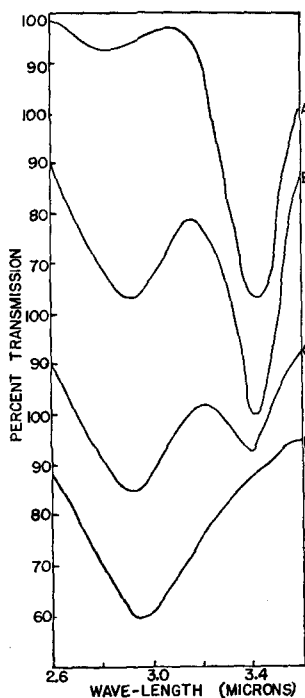


FIG. 4. Percentage transmission of phenol in ethyl acetate: *A*, pure ethyl acetate, cell thickness 0.007 cm; *B*, phenol 0.23 mole/lit., cell thickness 0.007 cm; *C*, phenol 0.95 mole/lit., cell thickness 0.003 cm; *D*, phenol 8 mole/lit., cell thickness 0.001 cm.

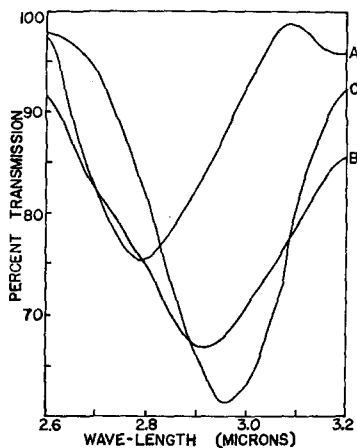


FIG. 5. Ratio of the transmission of a 0.007 cm layer of 0.23 mole/lit., solution of phenol to that of an equally thick layer of the pure solvent: *A*, phenol in benzene; *B*, phenol in ethyl acetate; *C*, phenol in dioxane.

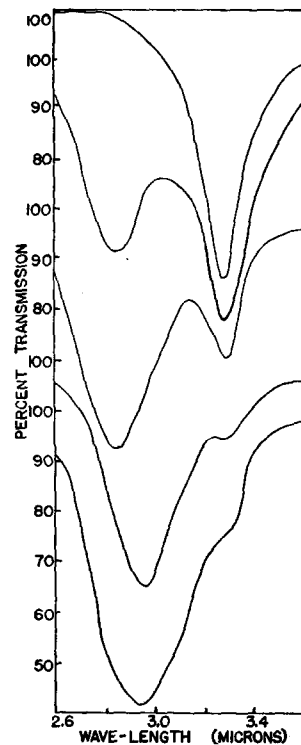


FIG. 6. Percentage transmission of phenol in nitrobenzene: *A*, pure nitrobenzene, cell thickness 0.007 cm; *B*, phenol 0.32 mole/lit., cell thickness 0.007 cm; *C*, phenol 1.2 mole/lit., cell thickness 0.003 cm; *D*, phenol 6 mole/lit., cell thickness 0.001 cm; *E*, phenol 9 mole/lit., cell thickness 0.001 cm.

twice. Instruments of the type used have been previously described.<sup>7</sup> Cell windows were of rocksalt; the thickness of the absorbing layer was maintained by mica washers. In order to bring out the OH band the cell thickness was increased as the phenol concentration was decreased. The maximum thickness was used in obtaining comparison curves of the pure solvents. At each setting of the prism circle, galvanometer deflections were taken with the cell in and with the cell out of the beam, the latter reading being made with a rocksalt plate in the beam to compensate for any scattering or absorption of the cell windows.

The results obtained for phenol in benzene are given in Fig. 1. The bottom curve represents the transmission of the most concentrated solution,

8 mole/lit. In this curve there appears a strong band with maximum of absorption at about  $2.96\mu$ , and this we attribute to the OH of the phenol. The less intense band, at  $3.28\mu$ , is characteristic of the CH group. For the 5 mole/lit. solution, second curve from the bottom, the positions of the bands apparently have not changed although the ratio of their intensities has changed. The vibrational band of the CH group of the solvent, benzene, appears at approximately the same position as the phenolic CH band. Therefore the band at about  $3.28\mu$  would not be expected to decrease with the phenol concentration as does the OH band. Actually the CH band is stronger for the lower concentrations because of the increase in cell thickness. The OH band for 0.95 mole/lit. seems to be double, with one component appearing at the usual position of  $2.96\mu$  and the other at shorter wave-lengths. The curve for 0.23 mole/lit. shows

<sup>7</sup> D. S. McKinney, C. E. Leberknight, and J. C. Warner, *J. Am. Chem. Soc.* **59**, 481 (1937); W. Dahlke, *Zeits. f. Instrumentenk.* **57**, 18 (1937).

only one maximum, which is at  $2.79\mu$  approximately. Diluting the solution has apparently effected a shift to the shorter wave-lengths of some  $0.17\mu$  in the OH band. The top curve, which is for pure benzene, indicates that the solvent has no band that would cause falsification by overlapping the hydroxyl band. Fig. 2 shows that the OH band varies in a similar way when the solvent is bromobenzene. It is not likely that bromine is able to share the proton with the oxygen of the OH,<sup>1</sup> and benzene itself has no donor. Hence, neither of the above solvents would be expected to form hydrogen bridges with the solute. The shift of the OH band to the shorter wave-lengths no doubt indicates the breaking of hydrogen bonds between the phenol molecules, the band at  $2.96\mu$  being caused by the associated OH and that at  $2.79\mu$  by the OH of single molecules.

One may expect the formation of hydrogen bonds with the OH to decrease the binding force between the H and O and hence to effect a shift of the OH band to the longer wave-lengths. The shift reported here for phenolic OH is hardly as great as that observed for alcoholic OH in carbon tetrachloride solution;<sup>2</sup> this difference suggests that the bonds between the phenol molecules are slightly weaker.

If the hydrogen bridges between phenol molecules are not as strong as the corresponding bridges between alcohol molecules, the breaking of the bridges in phenol may be expected to occur at higher concentrations. Lassettre<sup>1</sup> has pointed out that a small amount of hydrogen-bond-forming compound in the solvent materially decreases the polymerization of solutes associated through hydrogen bridges. Thus a small amount of water in the solution may affect measurably the concentration at which single molecules occur. The same is true for the measurements which have been made on alcohols. It should be mentioned that at the time the measurements which are reported here were taken high humidity made it impossible to prepare the solutions and cells without allowing some water to enter the solution, although special precautions were taken to prevent it. Such factors necessarily make measurements of this type somewhat qualitative.

The variations with dilution of the OH band of phenol in oxygenated solvents differ from that

discussed above for the solvents, benzene and bromobenzene. For the most concentrated solutions of phenol in all the solvents, however, the position of the band is approximately the same. Fig. 3 shows the results of a study of a series of solutions of different concentrations of phenol in dioxane. For 0.23 mole/lit., the most dilute solution employed, the position of the band is still very nearly  $2.96\mu$ , although the intensity is somewhat greater than it is for the corresponding concentration of phenol in benzene. It does not seem likely that this failure of the OH band to shift to the shorter wave-lengths, as it does when the solvent is benzene, means that the phenol is still highly associated at this concentration. Other measurements<sup>4, 8</sup> indicate that oxygenated solvents like dioxane have a greater tendency to decrease the polymerization of solutes of this type than does benzene. This tendency no doubt is due to the ability of the oxygenated solvents to combine with the solute through the formation of hydrogen bonds. If, when the hydrogen bridges are broken between the solute molecules, similar bridges are formed between the solute and solvent molecules, there may be no measurable effect on the OH band, or there may be a shift of the band to higher or lower frequencies, depending upon the strength of the newly-formed bonds as compared to that of the bridges which were broken between the solute molecules. In any case, however, if hydrogen bonds are formed, the position of the OH band would be at wave-lengths longer than for the OH of single molecules. The band appears at slightly shorter wave-lengths in dilute solution in ethyl acetate, Fig. 4, than it does for the most concentrated solutions, but at wave-lengths longer than for the dilute solution in benzene. Furthermore, as was the case for solutions in dioxane, the band is more intense than for the same concentration in benzene.

In Fig. 5 the absorption curves for 0.23 mole/lit. of phenol in dioxane, in ethyl acetate, and in benzene are compared. The absorbing layer was of the same thickness for all three solutions. Each curve represents the ratio of the transmission of the solution to that of an equal thickness of the pure solvent.

<sup>8</sup> C. J. Wilson and H. H. Wenzke, *J. Chem. Phys.* 2, 546 (1934).

In dilute nitrobenzene solution, Fig. 6, the phenolic OH band appears at wave-lengths only slightly longer than it does in dilute benzene solution. In view of this fact one may predict that the hydrogen bridges between phenol and nitrobenzene, if indeed they form at all, are rather weak. Some may prefer to think of this, as well as the other cases of hydrogen bonding dis-

cussed here, not as the formation of definite complexes but merely as a special orientation of the molecules due to proton attraction.

The writers wish to express their thanks to Dr. H. H. Nielsen for the use of his laboratory facilities and for his constant interest in this work, and to Dr. Alpheus W. Smith for his generous support.

JANUARY, 1938

JOURNAL OF CHEMICAL PHYSICS

VOLUME 6

## Potential Energy Curve of the Excited State of LiH

E. J. ROSENBAUM

*Department of Chemistry, University of Chicago, Chicago, Illinois*

(Received November 8, 1937)

A method developed by Klein has been applied to obtain the potential energy curve of the excited electronic state of LiH (state  $V$ ). This curve crosses the Coulombic curve of  $\text{Li}^+\text{H}^-$  and indicates dissociation of excited LiH into  $\text{Li}(^2P) + \text{H}$ . The effect of this behavior on Mulliken's explanation of the unusual shape of the state  $V$  curve is discussed. The interaction of the  $\text{Li}^+\text{H}^-$  and  $\text{Li}(^2P) \cdot \text{H}$  curves at moderately large interatomic distances is larger than Mulliken's estimate.

A PROCEDURE for obtaining the potential curve of a diatomic molecule to a sufficient degree of approximation and without the expenditure of an undue amount of time is highly desirable. The power series expansion in terms of the displacement of the atoms from their equilibrium position converges poorly for even moderately large displacements. While the Morse function is probably a fairly good approximation for most curves, for some abnormal ones, such as the curve considered here, it is useless and attempts to modify it can scarcely be expected to offer much improvement. Other types of potential functions have been suggested, but these frequently involve so many parameters that their applications are limited.

O. Klein<sup>1</sup> has given a semi-graphical method for obtaining the curve of a molecule directly from its observed energy levels. So far as the author is aware, this method has been applied only by Rydberg.<sup>2</sup> Since Rydberg has published no details of the application of the Klein method, it may be appropriate to discuss it somewhat fully.

<sup>1</sup> O. Klein, *Zeits. f. Physik* **76**, 226 (1932).

<sup>2</sup> R. Rydberg, *Zeits. f. Physik* **80**, 514 (1933).

Klein derives the following equation on the basis of classical mechanics:

$$S(U, \kappa) = \frac{1}{\pi(2\mu)^{1/2}} \int_0^{I'} (U - E(I, \kappa))^{1/2} dI,$$

in which  $U$  is a suitable value of the potential energy of the molecule,  $E(I, \kappa)$  represents the energy of vibration and rotation as a function of the action variable  $I$  and the quantity  $\kappa$  (equal to  $P^2/2\mu$ ),  $P$  is the angular momentum of the molecule,  $\mu$  is its reduced mass, and  $I'$  is that value of  $I$  for which  $U = E$ . As Klein suggests, it is probably a good approximation to replace  $I$  and  $\kappa$  by their quantum-mechanical equivalents,  $(v + \frac{1}{2})h$  and  $(K(K+1)h^2)/(8\pi^2\mu)$ . The maximum and minimum values of the interatomic distance for a molecule vibrating with the energy  $U$  are then given by

$$r_1, r_2(U) = (f/g + f)^{\pm 1/2},$$

in which  $f = (\partial S / \partial U)$  and  $g = -(\partial S / \partial \kappa)$ . With  $r_1$  and  $r_2$  known for each of a series of  $U$  values, the curve for  $U$  as a function of  $r$  can be plotted. If the  $U(r)$  curve for the rotationless state is wanted, the values  $f = (\partial S / \partial U)_{\kappa=0}$  and  $g = -(\partial S / \partial \kappa)_{\kappa=0}$  are to be used.