The OH-Vibration Spectrum in the Photographic Infrared.

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The result of our dipole measurement on ortho-substituted phenols(1) is in accordance with Pauling's theory(2) of quantum mechanical resonance, which was originally put forward for the interpretation of the infrared absorption spectra observed by Wulf and Liddel.(3) To supply further experimental evidence to this conclusion as well as to complete our former research(4) on the vibration spectra of alcohols, we have

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(1) Mizushima, *J. Chem. Soc. Japan*, **57** (1936), 936; see also Mizushima, Morino, and co-workers, *Physik. Z.*, **35** (1934), 905; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159; **29** (1936), 63, 111, 188.

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

(3) Wulf and Liddel, *J. Am. Chem. Soc.*, **57** (1935), 1464; Wulf, Liddel, and Hendricks, *ibid.*, **58** (1936), 2287.

(4) Mizushima, Morino, and Okamoto, this Bulletin, **11** (1936), 553, 698.

studied the overtones of the OH vibration as absorption spectra in the photographic infrared. The measurement was carried out with a glass spectrograph of our own construction which has a dispersion of 74 A per mm. at 9000 Å, iron and barium lines being used as reference. The samples were Kahlbaum's products, which were purified by redistillation or recrystallization. The accompanying table contains the experimental results obtained for carbon tetrachloride solutions of the concentration of 0.5 mol. We have also measured the absorption spectra in the pure liquid or fused state and found that some of the bands are changed in frequency as well as in intensity.(5) We shall, however, confine ourselves to the discussion of the experimental data obtained for the dilute nonpolar solutions, in which the normal vibration of a solute molecule is not greatly affected by the surrounding solvent molecules.(6)

Frequencies (cm.$^{-1}$) of Absorption Maxima of OH Vibration Bands.

(Solvent: CCl_4)

Substance	ν_2	ν_3	$x\omega$	ω	ν_1		D
					calc.	obs.	
CH_3OH	10424 (9593 Å)	13557 (7376 Å)	85	3816	7120	7120	116
C_2H_5OH	10394 (9621 Å)	13493 (7411 Å)	91	3830	7112	7090	109
n-C_3H_7OH	10388 (9626 Å)	13493 (7411 Å)	89	3820	7104		111
n-C_4H_9OH	10406 (9610 Å)	13459 (7430 Å)	104	3884	7144		98
C_6H_5OH	10332 (9679 Å)	13430 (7446 Å)	87	3790	7061	7050	113
p-C_6H_4ClOH	10322 (9688 Å)	13430 (7446 Å)	83	3773	7047		116
o-C_6H_4ClOH	10094 (9907 Å) st.*	13122 (7621 Å) st.	84	3701	6897	6910	110
	10323 (9687 Å) w.	13430 (7446 Å) w.	84	3775	7049	7050	116
o-C_6H_4BrOH	10005 (9995 Å) st.	12970 (7710 Å) st.	93	3705	6855	6860	100
	10328 (9682 Å) w.	13401 (7462 Å) w.	92	3812	7070	7050	106
o-$C_6H_4CH_3OH$	10328 (9682 Å)	13430 (7446 Å)	85	3783	7055	7060	114

* st. means strong intensity and w. weak intensity.

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(5) Measurements with alcohols in the pure liquid state were already carried out by several investigators, among which Freymann (Thèse Paris, 1933) gave experimental values close to those of our second overtones.

(6) The absorption bands at 9500Å of alcohols in the vapour state recently observed by Badger and Bauer (*J. Chem. Phys.*, **4** (1936), 711) have larger frequencies owing to the difference in the state of aggregation.

Let the vibrational level of the quantum number v be approximately expressed as

$$G(v) = \omega\left(v+\frac{1}{2}\right)-x\omega\left(v+\frac{1}{2}\right)^2 \tag{1}$$

Then the frequency of infinitesimal vibration ω and the anharmonicity factor x can be calculated, if we assign our observed bands to the second (ν_2) and third overtones (ν_3) of the OH vibration respectively. Using the values of ω and x *thus* evaluated, we have calculated the frequencies of the first overtone (ν_1) and compared them with the experimental values which Wulf and his co-workers(3) obtained in the same solution (sixth column of the table). The agreement is satisfactory within the limit of experimental error, so that the assignment of the absorption bands given above is proved to be correct.

By the extrapolation method the dissociation energy is calculated as

$$D = \frac{(\omega-x\omega)^2}{4x\omega} \tag{2}$$

which we can now evaluate by the use of ω and x given in the table. The calculated values (in Kcal.) shown in the last column of the table are in good agreement with those obtained from the thermochemical data (106 Kcal. for alcohols). Of course the comparison between these two kinds of dissociation energy is of no significance, if there is any complication of the electronic levels such as the crossing of them, but for these substances such does not seem to be actually the case.

Thus the experimental results obtained here together with all the other evidence available at present are consistent with the interpretation of these spectra to be due to one normal mode of vibration of the molecule, which is essentially the vibration of the hydrogen atom of the OH radical relative to the rest of the molecule. The two frequencies observed in all of the overtones for the ortho-halogenated phenols can therefore be ascribed to the stereoisomers I and II respectively,(7) which owe their existence to the quantum mechanical resonance between single and double bonds

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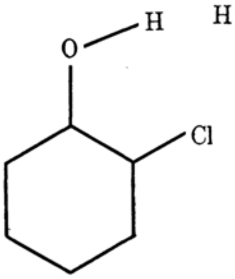
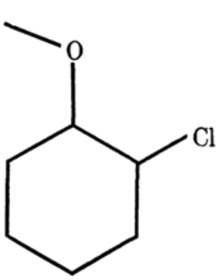
(7) The frequency which is approximately equal to that of phenol is assigned to the isomer II, in which the OH vibration is not affected by the halogen atom appreciably.

as suggested first by Pauling.(2) The absorption intensity for I is much larger than that for II, indicating that the number of molecules of the type I is much larger than that for II in conformity with the experimental result obtained in the dipole measurement.(1)



(I)



(II)

We have also observed a very interesting fact that the absorption intensity due to the OH vibration becomes very strong as compared with that due to the CH vibration in the dilute CCl_4 solution, while both of them do not seem much different in the pure liquid state.(8) This can be explained by assuming the association caused by hydrogen bond, which has a large effect in decreasing the intensity of a vibration spectrum.(9) Owing to the large difference in the polar character the inherent absorption intensity of the OH vibration must be much larger than that of the CH vibration as was actually observed in the dilute nonpolar solutions, but the considerable formation of hydrogen bond in the pure liquid state decreases the intensity of the former, so that it becomes comparable with (in some cases weaker than) that of the latter.

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(8) In some cases the absorption due to the CH vibration is much stronger than that due to the OH vibration in the pure liquid state.

(9) For *o*-nitrophenol we could not observe the second and third overtones of the OH vibration, just as Wulf and Liddel did not in the first overtone. This is ascribed to the formation of a hydrogen bond.(3)