The OH-Vibration Spectrum in the Photographic Infrared. II.

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In our previous work[1] we studied the near infrared absorption bands of monovalent alcohols and ortho-substituted phenols in the liquid state as well as in carbon tetrachloride solutions. The present paper deals with the investigation extended to the vapours of these substances. The experimental apparatus was essentially the same as that described in our

(1) Mizushima, Uehara, and Morino, this Bulletin, **12** (1937), 132.

previous paper, except that a three-meter absorption tube of glass was used.

The observed wave lengths of absorption maxima corresponding to the second and third overtones are shown, respectively, in the second and fourth columns of Table 1. Our values for the second overtone are in

Table 1. Wave length (Å) of absorption maxima of OH vibration bands.

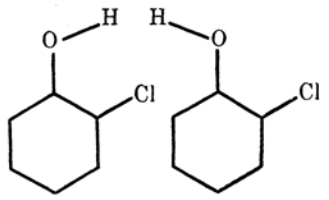
Substance	ν_2		ν_3	
	Vapour	Solution	Vapour	Solution
CH_3OH	9473 9514	9593	7282 7311	7376
C_2H_5OH	9533	9621	7323	7411
n-C_3H_7OH	9510 9557	9626	7304 7353	7411
n-C_4H_9OH	9511 9557	9610	7308 7356	7430
HCOOH	9773 9815	— —	7513 7534	— —
CH_3COOH	9760	—	7501	—
C_2H_5COOH	9761	—	7502	—
C_6H_5OH	9564	9679	7345	7446
o-C_6H_4ClOH	9568 9812	9687 9907	7346 7569	7446 7621
o-C_6H_4BrOH	9564 9884	9682 9995	7346 —	7462 7710
C_2H_4ClOH	9486 9538 9646	9595 9726	7287 7334 7429	— — —

general in good agreement with those of Badger and Bauer,[2] Herzberg and Verleger,[3] and Naherniac,[4] so far as the comparison can be made. For methyl alcohol Badger and Bauer[5] carried out also high dispersion measurement in the region of the third overtone.

The two absorption maxima observed for some alcohols and acids probably belong to different branches of the same vibration band, while those for ortho-halogenated phenols which have much larger wave length differences correspond to different bands of the two molecular species

(2) Badger and Bauer, *J. Chem. Phys.*, **4** (1936), 711.
(3) Herzberg und Verleger, *Phyik. Z.*, **37** (1936), 444.
(4) Naherniac, *Ann. phys.*, **7** (1937), 528.
(5) Badger and Bauer, *J. Chem. Phys.*, **4** (1936), 469.

given by the quantum mechanical resonance[1][6][7] (see Fig. 1). Of the two absorption maxima observed for the latter substances, that having the wave-length nearly equal to that of phenol is assigned to configuration II of Fig. 1 in which the interaction between OH and Cl is much smaller than that expected in the alternative configuration. The relative number of molecules in configuration II is, however, much smaller than that expected from the intensity ratio of the said two absorption maxima, as was shown by our previous dipole measurement.[8] This is due to the interaction between the chlorine and the hydroxyl hydrogen which reduces the absorption intensity of OH vibration considerably. The wave lengths of absorption maxima found for acids are much longer than those for alcohols, which indicates that practically all the molecules of acids assume configuration I of Fig. 2. This results is in conformity with the conclusion from the dipole measurement.[9][10]



I II

Fig. 1.

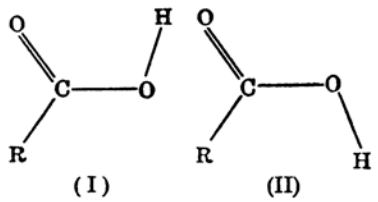
The absorption maxima observed for vapours have longer wave lengths by ca. 100 Å than those for the dilute carbon tetrachloride solutions[11] (third and fifth columns of Table 1). This fact is interesting when compared with the observation of Errera and Mollet[12] that for the fundamental tone the absorption maximum of the vapour of C_2H_5OH has practically the same wave length as that of the carbon tetrachloride solution. The effect of solvent molecule is, therefore, much larger for a higher quantum state than that for a lower one.

For ethylene chlorhydrin we observed three absorption maxima ($\nu_2^a = 9486$ Å, $\nu_2^b = 9538$ Å, $\nu_2^c = 9646$ Å) in the vapour state and two ($\nu_2^d = 9595$ Å, $\nu_2^e = 9726$ Å) in dilute carbon tetrachloride solutions. From the experimental results obtained for the other substances shown in Table 1, it may be considered that ν_2^a and ν_2^b correspond to ν_2^d and ν_2^c to ν_2^e. It is possible that these two absorption regions of ethylene chlorhydrin may have an explanation similar to that applied to the ortho-halogenated phenols. From the observed values of dipole moment[13] it

(6) Wulf and Liddel, *J. Am. Chem. Soc.*, **57** (1935), 1464; Wulf, Liddel, and Hendricks, *ibid.*, **58** (1936), 2287.
(7) Pauling, *J. Am. Chem. Soc.*, **58** (1936), 94.
(8) Kozima and Mizushima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **31** (1937), 296.
(9) Zahn, *Phys. Rev.*, **37** (1931), 1516; *Trans. Faraday Soc.*, **30** (1934), 804.
(10) Mizushima, *J. Chem. Soc. Japan*, **57** (1936), 936.
(11) In our previous communication we calculated the frequency of infinitesimal vibration ω and the anharmonicity factor x from our experimental values for the second and third overtones, putting the vibrational level of the quantum number v as

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

Using ω and x thus obtained we can calculate the frequencies of the fundamental tone and first overtone for C_2H_5OH as 3648 cm.$^{-1}$ and 7114 cm.$^{-1}$ respectively, both of which are in good agreement with the experimental values of Errera and Mollet (3640 cm.$^{-1}$) and Wulf and Liddel (7090 cm.$^{-1}$).
(12) Errera and Mollet, *Nature*, **138** (1936), 882; *Compt. rend.*, **204** (1937), 259.
(13) Zahn, *Physik. Z.*, **33** (1932), 525.



(I) (II)

Fig. 2. The two molecular configurations of carboxylic acids expected from the quantum mechanical resonance.

Table 2. Wave length variation of absorption maximum of ethylene chlorhydrin with concentration.

1 : x*	Wave length (Å) of absorption maximum.	
pure liquid	9760	—
1 : 1	9755	—
1 : 4	9731	—
1 : 8	9724	9621
1 : 16	9724	9616
1 : 80	9725	9609
1 : 300	9726	9595
vapour	9646	9538, 9486

* The solution consists of one part by volume of ethylen chlorhydrin and x parts of carbon terachloride.

is concluded that the molecular configuration of ethylene chlorhydrin corresponds either to the trans form $\overset{Cl}{\diagdown}CH_2-CH_2\overset{OH}{\diagdown}$ or to the cis form $Cl\diagdown CH_2-CH_2\diagup OH$, but it is not unreasonable to assume the coexistence of these two forms, since the change in abundance ratio does not affect the apparent value of dipole moment. Then ν_2^a and ν_2^b (ν_2^d in solution) can be assigned to the trans form and ν_2^c (ν_2^e in solution) to the cis form, as the former will have wave lengths not much different from those of alcohols owing to the smaller interaction between Cl and OH. This assignment is in conformity with the behaviours of these bands in carbon tetrachloride solutions as stated in the following (see Table 2). In the liquid state and in concentrated solutions we observed a broad band around $\lambda = 9760$ Å, which on dilution becomes sharper and is shifted towards higher frequency region until the absorption maximum attains the wave length of 9726 Å, i.e. ν_2^c of the cis form. From a certain dilution on there appears in the shorter wave length region another band, which we have assigned to the trans form (ν_2^d). In other words the OH vibration of the cis form can be observed in all the conditions mentioned above, while that of the trans form only in the dilute solutions and in the vapour. This fact is just what we would expect from the configurations of these two molecular species, since the trans form will easily form *intermolecular* hydrogen bond (such as in the case of alcohols)[14] and therefore the OH vibration of a single molecule can hardly be observed in concentrated solutions, while there is much less probability for such bonding for the cis form whose hydroxyl hydrogen is coupled with the chlorine in the same molecule.

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(14) According to Errera and Mollet[12] the OH band due to the isolated molecule of ethyl alcohol can be observed only in dilute solutions.