

On the Question of the Intra and Intermolecular "Hydrogen Bond" and the Absorption Spectra in the Near InfraRed

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Vapor-Liquid-Solution Displacements in Vibration Absorption Bands

To aid us in an interpretation of the structure of the absorption bands of water molecules in CS_2 and CCl_4 solutions and during other studies we have made observations on the displacements of certain relatively sharp infra-red absorption bands. A graphical summary of some of the data is given in Fig. 1. The $\Delta\nu$ wave number shifts are given with

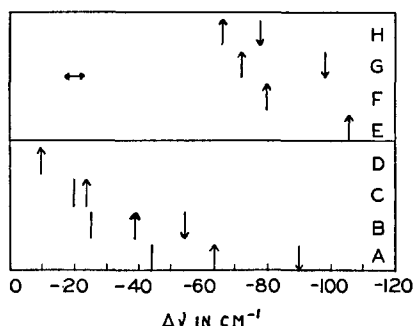


FIG. 1. Wave number displacements from vapor positions. A-D: CH bands. E-H: OH bands. A: chloroform, 1.145 μ ; B: chloroform, 1.680 μ ; C: ethyl alcohol, 1.730 μ ; D: formic acid, 1.721 μ ; E: formic acid, 1.435 μ ; F: ethyl alcohol, 1.395 μ ; G: water vapor (unresolved Q branch), 1.379 μ ; H: water vapor (unresolved Q branch), 1.875 μ .

respect to the vapor positions. Upward arrows, downward arrows and simple lines indicate CCl_4 solution, CS_2 solution and pure liquid displacements, respectively. The concentrations of the solutions were not the same; the greatest concentration was 0.86 mole per liter in ethyl alcohol. The length of the double-headed horizontal arrow indicates the half-slit-width in wave numbers, 5 cm^{-1} , corresponding to 0.2 mm on the record plate. A shift of this amount can be observed easily by the superposition of two transparent records.

The figure reveals the following facts:

(1) A comparison of displacements in A-D with those in E-H indicates that in general band positions of the CH type are less dependent upon the surrounding medium than are those of the OH type.

(2) Comparisons of A with B, and of G with H, indicate a dependence of shift upon the magnitude of the frequency.

(3) The shifts are greater in the nonpolar solvents than in the pure liquids.

(4) In every instance CS_2 has a greater effect than CCl_4 .

J. W. ELLIS

E. L. KINSEY

University of California,
Los Angeles, California,
July 13, 1938.

On the Question of the Intra- and Intermolecular "Hydrogen Bond" and the Absorption Spectra in the Near Infra-Red

A large number of publications have appeared particularly in this journal, on the information given by the absorption spectra in the near infra-red in regard to inter- and intramolecular bonds. Many authors do not seem to know of the researches we have pursued on this subject since 1932 in Professor Cotton's laboratory, Paris, with the help of several co-workers: Mrs. Marie Freymann, MM. P. Barchewitz, J. Guéron, A. Naherniac, B. Vodar, Yeou Ta and others. We think therefore that we should sum up the main results we obtained, with reference to the original publications.

In 1932¹⁰ we have shown that the absorption spectra in the near infra-red permit the study of the phenomena of molecular associations: by heating (or diluting in CCl_4 for instance) an alcohol or an acid, we have shown that the intensity of the characteristic band of the OH nonassociated groups increases; this essential result has been mentioned several times since by many authors. Later researches, made by Errera and his co-workers,⁵ by ourselves¹⁵ . . . have extended our results and confirmed Barchewitz' suggestions.² In alcohols, for instance, there are at least two OH bands: the one, we have called $(\text{OH})_v$, characteristic of the nonassociated OH groups, as in vapor; it is the sharp band we have studied, the intensity of which increases with the temperature. The other, called $(\text{OH})_s$, characteristic of the associated OH groups, as in solid, a very broad band, the intensity of which decreases when the temperature increases.

The appearance of this latter band is connected with the phenomenon of so-called "hydrogen bonds" (3, 4, 6, 14, etc. . . .). In a note to the *Bulletin Société Chimique de France*¹⁴ we have distinguished, as follows, the intra- and intermolecular bonds.

Intramolecular "hydrogen bond"

- { Chelation^{12, 18}
 Ketone-enol isomerism^{12, 18}
 Amide tautomerism¹²

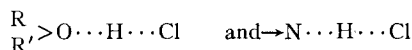
Intermolecular "hydrogen bond"

- { Bond between the molecules of two different substances { oxonium compounds { with HOR (Aceton, dioxan, ...) ^{12, 15}
 with HCl (aether, alcohol, ...) ¹⁶
 ammonium compounds { with HOR (Amines, nitrils, ...) ¹³
 with HCl¹¹
 Bond between the molecules of the same substance { Alcohols, acids^{10, 15}
 Oximes¹²
 Hydrogen chloride liquefied gas¹⁷
 (molecular association)

Let us emphasize a few points:

In the intramolecular bond (chelation, ketone-enol isomerism) the (OH)_v band disappears as Wulf, Liddel and their co-workers have shown;⁷ but (OH)_s appears¹⁸ reversing certain erroneous experimental results. Our work, with Mrs. Freymann, has shown that, contrary to the classical chemical formula of the tautomerism of amides, the (OH)_v band does not appear and the (NH) band is weak.¹²

For the intermolecular bonds between different substances, the numerous examples we have given^{13, 15} seem to be based upon experimental data more precise than the interesting researches made by Gordy at the same time. We add that the *hydrogen chloride solutions*



(two examples we think we can compare) do not appear to have been studied so far. As to the "*phenomenon of dissimulation for the tetracoordinated nitrogen*," we refer to our general work¹² and to the thesis of Mrs. Freymann (in print). We mention only that, in a quite general way the

(NH) band disappears or decreases in the aqueous solutions in which nitrogen is tetracoordinated. For instance NH₄⁺ Cl⁻, RNH₃⁺ Cl⁻, NH₃⁺ CH₂COO⁻ [Co (NH₃)₅ / H₂O] Cl₃, . . . (refer also to Edsall).^{4'}

For the intramolecular bonds between molecules of the same substance, our researches^{10, 15} and Naherniac's studies⁹ do not seem to have been noticed by Badger and Bauer¹ who, besides, have thoroughly confirmed our own results.

The example of the oximes $\begin{matrix} R \\ R' \end{matrix} > C = N - OH$ ^{12'} supplies another instance of molecular association that had not yet been observed. Finally, we have just shown with Mr. Vodar and Mr. Yeou Ta that liquefied HCl presents two vibration bands, one characteristic of the nonassociated molecules (second harmonic about 1.22μ), the other characteristic of the associated molecules (about 1.29μ); the latter decreases when the temperature increases from -80 to +14°C, which shows the *association of liquefied HCl*.¹⁷

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 Paris, France,
 July 1, 1938.

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