

# HYDROGEN BONDING IN ALCOHOLS, ACIDS AND SECONDARY AMIDES

(Electrostatic Interaction and Resonance)

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## I. INTRODUCTION

COGGESHALL<sup>1</sup> has calculated the shift in the free hydroxyl stretching frequency of methanol due to intermolecular association, treating hydrogen bonding as an electrostatic interaction. The difference between the calculated and recorded frequencies is about  $65 \text{ cm.}^{-1}$  which appears to be considerable. In alcohols, the intermolecular associations are of  $\text{H} \dots \text{O} - \text{H} \dots \text{O}$  type in their polymeric state. In acids the functional groups responsible for hydrogen bonding are hydroxyl and carbonyl linkages and in secondary amides, they are the amino and the carbonyl linkages giving rise to hydrogen bonding of the type  $\text{O} - \text{H} \dots \text{O} = \text{C}$  and  $\text{N} - \text{H} \dots \text{O} = \text{C}$  respectively. In the earlier work<sup>2</sup> the authors have calculated the shift in the N—H symmetric stretching frequencies of primary amides, taking into consideration the resonance structures of these molecules and the double bond character of  $\text{C} = \text{O}$  and  $\text{C} - \text{N}$  linkages. In the present paper the free OH and NH stretching frequencies of alcohols, acids and secondary amides, as recorded by various workers<sup>1, 3-9</sup> have been used to calculate the corresponding bonded stretching frequencies. The average values of the OH stretching frequencies are used for calculations in cases where they are recorded by more than one worker as in the case of methanol and acetic acid.

## II. DISSOCIATION ENERGIES OF THE FREE OH AND NH LINKAGES

The OH or the NH stretching frequency is considered to be independent of the rest of the molecule. As a result of hydrogen bonding, the OH and the NH diatomic group is immersed in an electric field in the presence of oxygen atoms of the hydroxyl group in alcohols or carbonyl linkages in acids and amides of other molecules. Using Schrodinger's equation with a Morse

potential energy function, the frequency in  $\text{cm.}^{-1}$ , arising out of the transitions from the ground level to the next vibrational level, is given as

$$\nu = a/\pi c (D/2M)^{\frac{1}{2}} - a^2 h/4\pi^2 M c \quad (1)$$

$M$  is the reduced mass of the OH or the NH group and  $D$  is the dissociation energy of the linkages. The dissociation energy of the OH bond<sup>10</sup> is 110.6 K.cal./mole or  $7.71 \times 10^{-12}$  erg./molecule and its reduced mass is  $1.585 \times 10^{-24}$  gram. The corresponding values of the NH bond are 93.4 K.cal./mole or  $6.512 \times 10^{-12}$  erg./molecule and  $1.573 \times 10^{-24}$  gram respectively. With these values of 'D' and 'M' and the free OH stretching frequencies of methanol, ethanol, formic and acetic acids and the free NH stretching frequency of N-methyl acetamide, the constant 'a' is calculated in case of each compound as per expression (1). These values are given in Table IV.

### III. UNBALANCED CHARGES

The bond lengths, the O—H...O and the N—H...O distances of the alcohols,<sup>11-13</sup> acids,<sup>14-15</sup> and the secondary amides<sup>16</sup> are given in Table I.

TABLE I

*Bond lengths of alcohols, acids and a secondary amide in Å*

Bond	Methanol	Ethanol	Formic acid	Acetic acid	N-methyl acetamide
C—H	1.093	1.093	1.085	..	..
C—O	1.434	1.430	1.312	1.290	..
C=O	..	..	1.245	1.240	1.230
O—H	0.937	0.937	0.950	0.950	..
C—CH <sub>3</sub>	..	1.550	..	1.510	1.510
O—H...O	2.660	2.660	2.725	2.610	..
C—N	..	..	..	..	1.290
N—H	..	..	..	..	0.995
N—CH <sub>3</sub>	..	..	..	..	1.470
N—H...O	..	..	..	..	2.830

The bond moments of the different linkages in addition to those reported earlier<sup>2</sup> are<sup>1, 17</sup>

$$(O-H) = 1.5 \text{ D}, \quad (C-O) = 0.8 \text{ D}, \quad (N-CH_3) = 1.3 \text{ D}$$

The unbalanced charges in various atoms of compounds under investigation are indicated in Fig. 1 where X is H or CH<sub>3</sub>.

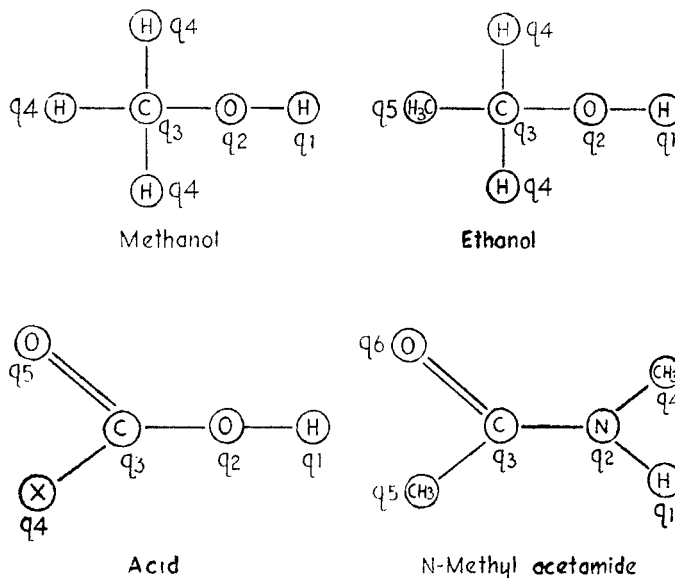


FIG. 1

The unbalanced charges on various atoms have been calculated as in the earlier work<sup>2</sup> by using  $\mu = qd$ , together with the expressions

$$\begin{aligned} q_1 + q_2 + q_3 + 3q_4 &= 0 && \text{for methanol,} \\ q_1 + q_2 + q_3 + 2q_4 + q_5 &= 0 && \text{for ethanol,} \\ q_1 + q_2 + q_3 + q_4 + q_5 &= 0 && \text{for formic acid and acetic acid,} \\ q_1 + q_2 + q_3 + q_4 + q_5 + q_6 &= 0 && \text{for N-methyl acetamide.} \end{aligned}$$

These values of unbalanced charges are given in Table III.

#### IV. REDUCTION IN THE IONIC CHARACTER OF THE BONDED OH AND NH LINKAGES

The bond energy due to ionic character of the OH or the NH linkage is obtained by using the known bond energies  $D(O-H)$ ,  $D(O-O)$ ,  $D(H-H)$ ,  $D(N-H)$  and  $D(N-N)$  in Pauling's postulate of the Additivity of Normal Covalent Bonds.<sup>2, 10</sup> The intermolecular associations in alcohols,

acids and secondary amides are represented in Fig. 2 (a), (b) and (c) respectively.

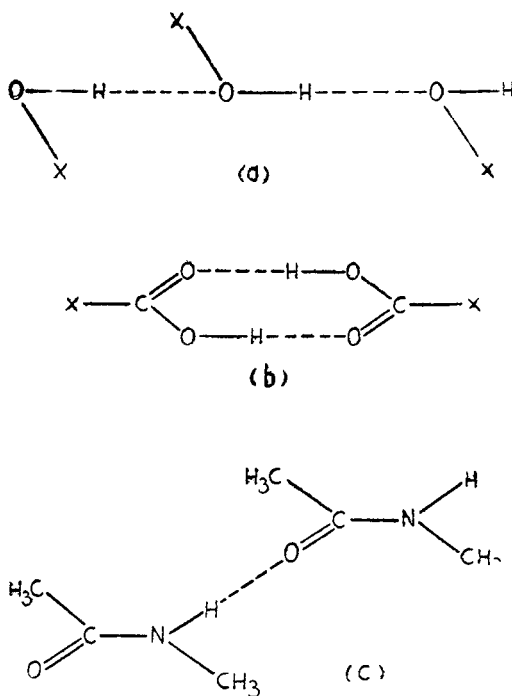


FIG. 2

As seen in Fig. 2 (a) in alcohols the fractional reduction in the ionic character of the OH linkage is obtained as the ratio of the electrostatic force  $F_1$  on the hydrogen atom due to the presence of the oxygen and the hydrogen atoms on either side of it as a result of hydrogen bonding, to that  $F_2$  due to the charge inequality in the OH group. On the other hand, in acids and amides  $F_1$  is the electrostatic force on the hydrogen atom due to just the oxygen atom of another molecule. From  $F_1/F_2 = 0.426$  for methanol and 0.4 for ethanol, the dissociation energy of the OH linkage of each molecule is calculated as per the expression

$$D' = 110.6 - 42 \times F_1/F_2 \text{ K.cal./mole} \quad (2)$$

The values of  $D'$  in erg/molecule are given in Table IV. These are used in (1) and the bonded OH stretching frequencies of methanol and ethanol are calculated. These are given in Table V. It is seen from these observations that the difference between the observed and the calculated frequencies is  $19 \text{ cm.}^{-1}$  in methanol and  $18 \text{ cm.}^{-1}$  in ethanol. This improvement in the calculated frequency of methanol as to the difference of  $65 \text{ cm.}^{-1}$  obtained

by Coggeshall is due to the fact that the electrostatic force  $F_1$  on the hydrogen atom of the hydroxyl group is obtained by the authors as due to the presence of the oxygen and the hydrogen atoms of the two neighbouring molecules as shown in Fig. 2 (a). Coggeshall on the other hand, has taken into consideration only the force on the hydrogen atom arising out of only the oxygen atom. In addition to this factor we have used the bond length data of methanol obtained from the analysis of its microwave spectrum<sup>11</sup> instead of that from the covalent radii of the atoms. Similar calculations in case of formic and acetic acids and N-methyl acetamide indicate a wide difference between the calculated and observed stretching frequencies as in our earlier work<sup>2</sup> in regard to the NH stretching frequencies of formamide and acetamide.

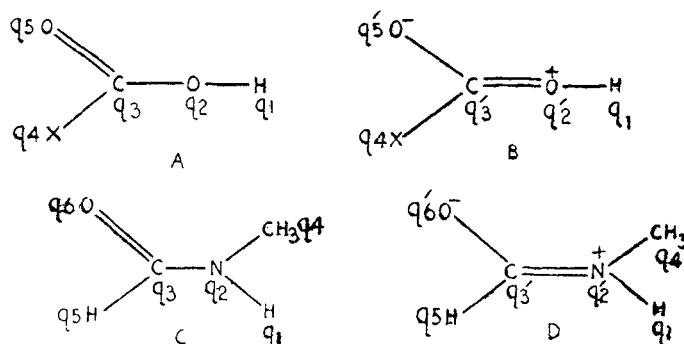


FIG. 3

TABLE II

*Double bond characters of different linkages of acids and s-amides*

Substance	Percentage of double bond character of		
	C=O	C—O	C—N
Formic acid	73	32	..
Acetic acid	78	43	..
N-methyl acetamide	88	..	70

V. RESONANCE STRUCTURES

The large differences between the observed and the calculated OH stretching frequencies of formic and acetic acids or of NH stretch of N-methyl aceta-

TABLE III  
*Unbalanced charges in different atoms (in  $10^{-10}$  e.s.u.)*

Unbalanced charge	Methanol	Ethanol	Formic acid		Acetic acid		N-methyl acetamide	
			Without resonance	With resonance	Without resonance	With resonance	Without resonance	With resonance
$q_1$	1.60	1.60	1.58	1.58	1.58	1.58	1.31	1.31
$q_2$	-1.64	-1.58	-0.32	-0.73	-0.27	-0.81	-0.41	-0.94
$q_3$	-1.07	-1.02	-0.34	-0.15	0.36	0.34	-0.09	-0.40
$q_4$	0.37	0.37	0.37	0.37	0.27	0.27	0.88	0.88
$q_5$	..	0.26	-1.93	-1.58	-1.94	-1.66	0.26	0.26
$q_6$	..	..	..	..	..	..	-1.95	-1.80

mide is due to the fact that there are two possible resonance structures of these molecules as indicated in Fig. 3.

In acids and amides the carbonyl bond does not have a 100% double bond character and the C—O and C—N linkages have considerable amount of double bond character. The double bond characters of these linkages have been obtained as earlier<sup>2</sup> and are given in Table II.

It is seen from Figs. 3 (A) and (B) that the unbalanced charges on the carbon, oxygen and nitrogen atoms of C—O, C=O and C—N linkages would be different in the two resonance structures. The unbalanced charges in those atoms for the structures B and D and the actual unbalanced charges on the different atoms in these molecules after taking resonance into consideration, have been calculated by the methods given earlier.<sup>3</sup> These are given in Table III.

Using these unbalanced charges thus obtained, the ratio  $F_1/F_2$  is calculated in case of each compound. The dissociation energies of the bonded OH linkage of formic and acetic acids, and the bonded NH linkage of N-methyl acetamide are calculated from the expressions

$$D_{\text{OH}} = 110.6 - 42 \times F_1/F_2 \text{ K.cal./mole}$$

$$D_{\text{NH}} = 93.4 - 22.1 \times F_1/F_2 \text{ K.cal./mole} \quad (3)$$

These dissociation energies in erg/molecule are given in Table IV.

TABLE IV

*Dissociation energies of the bonded OH and NH linkages in ( $10^{-12}$  erg/molecule) and the values of 'a' (in  $10^8 \text{ cm.}^{-1}$ )*

	Methanol	Ethanol	Formic acid	Acetic acid	N-methyl acetamide
D'	6.491	6.490	5.90	5.753	5.648
a	2.312	2.310	2.270	2.240	2.440

With these values of D' the OH bonded stretching frequency of formic and acetic acids and the bonded NH stretching frequency of N-methyl acetamide are calculated as per expression (1). These are given in Table V.

TABLE V  
*Calculated and observed OH and NH stretching frequencies  
 (in cm.<sup>-1</sup>)*

Substance	Observed free OH or NH stretch	Bonded OH or NH stretching frequency		
		Observed	Calculated	$\Delta\nu$
Methanol	.. 3625	3344	3325	+19
Ethanol	.. 3631	3338	3320	+18
Formic acid	.. 3570	3110	3103	+ 7
Acetic acid	.. 3535	3035	3025	+10
N-methyl acetamide	.. 3500	3280	3257	+23

## VI. SUMMARY

The free OH and NH stretching frequencies of methanol, ethanol, formic and acetic acids and of N-methyl acetamide are used to calculate the shift in their frequencies due to hydrogen bonding. These calculations are based on the fact that the hydrogen bonding is an electrostatic interaction and that the ionic character of the bond diminishes on hydrogen bonding. The observed and the calculated bonded stretching frequencies agree fairly in methanol and ethanol, but in formic and acetic acids and N-methyl acetamide, the agreement between the corresponding observed and calculated frequencies is obtained only when the two possible resonance structures in these molecules are taken into consideration for calculations.

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