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# On The Dependence of O-H Bond Length on The O-O Bond Length in Hydrogen Bonded O-H...O Systems

by

V. Ananthanarayanan

## Introduction

In recent times several experimental and theoretical studies on the hydrogen bonded O-H...O vibrations have been made. During the studies on such vibrations in carboxylic acids made by the author [1, 2], certain interesting evidences relating to the O-H bond length ( $r$ ) in monomeric and dimeric carboxylic acids were observed. The location of hydrogen atom positions by conventional x-ray diffraction methods is usually accompanied by uncertainties and thus the estimation of the O-H bond lengths by other methods capable of giving more certain bond lengths is of great interest.

## Vibrational Spectra Data

The lowering of the O-H stretching frequency ( $\nu_{OH}$ ) from its free or unbonded value of  $\approx 3600\text{cm}^{-1}$  in the vapor state to lower values due to the hydrogen bond formation is well known. Thus when the O-H...O bond length ( $R$ ) is about  $2.6 \text{ \AA}$ , the  $\nu_{OH}$  frequency is  $\approx 2000\text{cm}^{-1}$ . The correlation of the  $\nu_{OH}$  and  $R$  have been extensively used to judge the strength of the hydrogen bond.

Studies made on the vibrational spectra of carboxylic acids show that one observes characteristic frequency due to O-H bond at  $2.84\mu$  ( $3521 \text{ cm}^{-1}$ ) in monomers and at  $3.25 \mu$  ( $3073 \text{ cm}^{-1}$ ) in dimers, lowered due to the formation to the hydrogen bonds between the acid dimers.

## THE RELATION BETWEEN THE VALUES $r$ , $R$ and $\nu_{OH}$ IN HYDROGEN BONDED SYSTEMS

Empirical correlations of the interdependence of  $r$ ,  $R$  and  $\nu_{OH}$  values are available in the literature [3]. While many potential models which treats the vibrational spectrum of the hydrogen bridges are available, the one developed by Lippincott and Schroeder [4] is most successful in explaining the various aspects of O-H...O Systems. The author applied this model to explain the low frequency hydrogen bridge vibrations in carboxylic acids [1] with considerable success.

This force field visualizes the hydrogen bond to be made up of two bonds O (I) H . . (II) O where bond I is equivalent to a slightly stretched typical covalent bond and the bond II is a weak bond which is equivalent to a highly stretched bond. The hydrogen atom is located along the line of centers between the two oxygen atoms making up the bond and a repulsive Van der Waal's potential and an attractive electrostatic potential is assumed to exist between the two electronegative atoms of the hydrogen bond. Through the application of conditions describing a stable equilibrium the following expression has been derived by Lippincott and Schroeder:

$$r-r_0 = \left[ \left\{ \exp(-n^* [R-r-r_0^*]) \right\}^2 / 2(R-r) \right] \\ \div \left\{ \exp \frac{n(r-r_0)^2}{2r} \right\} \\ \times \left[ \frac{r^2 (R-r-r_0^*) (R-r+r_0^*)}{(R-r)^2 (r+r_0)} \right] \quad \text{---(1)}$$

where

$R$  = equilibrium O---O distance

$r_0$  = equilibrium length of  
bond I =  $0.96 \times 10^{-8}$  cm  
=  $r_0^*$  = equilibrium  
length of bond II

$n$  = a constant of  
potential function  
for bond I =  $9.18 \times 10^8$  cm $^{-1}$

$b$  = repulsion constant of the  
potential function =  
 $4.8 \times 10^8$  cm $^{-1}$

$r$  = length of bond I

$r^*$  = length of bond II =  $(R-r)$

$n^*$  =  $gn$ , where  $g = 1.45$ ,  
and  $n^*$  being the constant  
of potential function for  
bond II.

This equation is suitable for calculating  $\Delta r$  i.e.  $(r-r_0)$  as a function of  $R$  by the method of successive approximations. Similar expressions for the relationship between  $\angle \text{OH}$  and  $R$  have been reported and extensively used. For greater details the original papers should be referred to.

There are several ways in which the observed  $\angle \text{OH}$  frequencies could be used to calculate the OH bond lengths in monomers and dimers. First a diatomic model with the reduced mass of the O-H

bond could be used to calculate the stretching force constants ( $K_{OH}$ ) of the OH bonds in dimers and monomers. The simple relation for this is as follows:

---(2)

$$K_{OH} = 4\pi^2 C^2 \mu \nu_{OH}^2$$

where  $C$  = velocity of light

$\mu$  = reduced mass of the system

These values of  $K_{OH}$  could be substituted in the Badger's relation [5],

$$r_{OH} = \left( \frac{C_{ij}}{K_{OH}} \right)^{\frac{1}{3}} + d_{ij}$$

where  $C_{ij}$  and  $d_{ij}$  are constants, tabulated by Badger, which depend on the atoms forming the bond. The force constants were calculated to be  $6.85 \times 10^5$  dynes per cm in the monomers and  $5.21 \times 10^5$  dynes per cm in the dimers. Substitution of these values in the Badger's relation leads to the O-H bond length values of 0.98 Å in monomer and 1.04 Å in the dimers.

There is one very interesting evidence for such bond length changes available in literature. In the case of the diatomic O-H the vibrational and rotational constants for the electronic states are well known. Fortunately for two electronic states the values of the stretching frequencies and the internuclear distances are known very precisely [6]. They are as follows:  $3735 \text{ cm}^{-1}$  and 0.9706 Å in the  $2\pi_i$  state;  $3181 \text{ cm}^{-1}$  and 1.0121 Å in  $2\Sigma^+$  state. The "frequency difference"  $\Delta\nu_{OH} = 554 \text{ cm}^{-1}$  is fairly close to the case under consideration in our discussion. The value  $\Delta r$  for this change of frequency corresponds to 0.042 Å. Substitution of these frequencies in relation (1) gives the results that  $\Delta r$  could be as much as 0.044 Å for this order of change in OH frequencies. This is easily verified since  $\Delta r$  values for relation (1) as function of  $R$  and  $\nu_{OH}$  are tabulated at convenient intervals by Lippincott and Schroeder.

Due to favorable scattering factors of hydrogen atoms, neutron diffraction studies are of great help in locating hydrogen atom positions in molecules and crystals. Such studies on many O-H---O bonded crystals have been reviewed by Hamilton [7]. It had been proposed that the following type of relation connecting O-H and O---O bond lengths is generally valid:

$$r(\text{O-H}) = 1.574 - 0.2145R(\text{O---O}) \quad \text{---(3)}$$

Although precise, comparably accurate, individual O-H bond lengths for monomers and dimers are not available, it is well known that the O-H---O bonds in many carboxylic acid dimers are reported to be 2.65 Å long. The data used to formulate relation (3) has been also plotted in the form of smooth curve relating  $R$  and  $r$  by Pimentel among others [3].

Such curves predict that in a non bonded case O-H bond length is as low as 0.96Å. From these data also it seems the actual O-H bond length changes involved may be as much as 0.05Å.

### Conclusion

There seems to be considerable evidence derived from diverse types of experiments supporting the view that the O-H bond lengths in carboxylic acid dimers and monomers differ as much as 0.04Å.

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