Vol. 7 No. 1
Winter 1996

ONE-DIMENSIONAL TREATMENT OF HYDROGEN BOND

PART 1

THE CASE OF THE LINEAR HYDROGEN BOND

F. Milani-Nejad

Department of Chemistry, Ferdowsi University, Mashhad, Islamic Republic of Iran

Abstract

The one-dimensional model of Lippincott and Schroeder for hydrogen bond has been re-examined and it has been shown that O-H bond distance depends on repulsive van der Waals and attractive electrostatic potentials. It has been shown that constant b in the van der Waals repulsion potential is not transferable to all hydrogen bonds. The possibility of obtaining the semi-empirical parameters in the Lippincott and Schroeder potential function from OH stretching frequencies, hydrogen bond energy and geometrical parameters has been discussed.

Introduction

Among the numerous potential functions which have been used to describe the motion of the proton in the hydrogen bond [1-8], that proposed by Lippincott and Schroeder [2] for linear hydrogen bond is the one most often used in the evaluation of hydrogen bond energy and the calculation of OH stretching frequency, force constants, O-H bond distance and 0...0 distance [9-11].

Lippincott and Schroeder have proposed the following potential function for one-dimensional hydrogen bond.

$$V = D[1-\exp(-n(r-r_0^*)^2/2r)] - D^*\exp(-n^*(R-r-r_0^*)^2/(2(R-r)) + A[e^{-bR} - \frac{1}{2}(R_0/R)^m e^{-bR_0}] \qquad (1)$$

(For a detailed description of the terms used in this equation see Reference 2).

In our re-investigation of equation 1, we encountered an error in the calculation of the O-H bond distance and OH frequency as a function of R. These authors assumed that constant "A" in equation 1 did not depend on the O-H bond distance and therefore it was dropped from the calculatic of the first and second derivatives of equation 1 f calculation of O-H bond distance and OH stretching fr quencies. As we will show in this paper, the constant " does depend on O-H bond distance and this dependenc has a great influence on the calculation of O-H bor distance and on the OH stretching frequency.

Keywords: Hydrogen bond; H bond energy; H bond potential function

Calculation of O-H Bond Distance and OH Stretching Frequency

In equation 1, "A" is constant for a given value of R_0 a it has been shown by Lippincott and Schroeder that remains almost constant over a wide range of R_0. Th constant is determined from the equilibrium condition $(\partial V/\partial R)_{eq} = 0$, which leads to the following expression:

$$A = \frac{n^*D^*(R-r-r^*)(R-r+r_0^*)}{2(R-r)^2(b-mR_0/2)e^{-bR_0}}\exp(-n^*(R-r-r_0^*)^2/2(R- \qquad (2)$$

This equation clearly shows that A depends on r, t O-H bond distance. Substituting equation 2 into equati 1 leads to the following expression for potential functic

$$V=D[1-\exp(-n(r-r_0)^2/2r)]-D^*[\exp(-n^*(R-r-r_0^*)^2/2(R-r))]$$
$$+[\frac{n^*D^*(R-r-r_0^*)(R-r+r_0^*)}{4(R-r)^2(b-m/2R)}]\exp(-n^*(R-r-r_0^*)^2/2(R-r)) \qquad (3)$$

Since A was considered independent of r by Lippincott and Schroeder it was dropped from the first and second derivative of equation 1 with respect to r. The following expression was obtained from equilibrium conditions of $(\partial V/\partial r)_{eq}=0$ for calculation of O-H bond distance.

$$\Delta r=[\frac{r^2(R-r-r_0^*)(R-r+r_0^*)}{(R-r)^2(r+r_0)}][\frac{\exp(-n^*(R-r-r_0^*)^2/2(R-r))}{\exp(n(r-r_0)^2/2r)}] \qquad (4)$$

As a result of this assumption, the calculated O-H bond distance from equation 4 does not correspond to the minimum or maximum in the potential energy curve versus r as it should do. For example, for 0-0 distance of 2.45 Å the calculated O-H distance from equation 4 for the parameters suggested by Lippincott and Schroeder by method of successive approximation is 1.151 Å, whereas the potential energy curve versus r (equation 3) shows two minima at 1.079 and 1.438 Å and one maximum at 1.303 Å (see Fig. 1). For 0-0 distance of 2.40 Å the calculated O-H distance is the same as the one calculated from equation 1, but careful examination of the potential function versus r shows that the broad potential curve has two minima and the energy of the second minimum at 1.349 Å is 0.2 kcal/mol lower than the first one at 1.164 Å. If we choose the value of $b=5.0 \times 10^8 cm^{-1}$, then the first minimum will become slightly lower than the second one (Fig. 2).

From the first derivative of equation 3 and equilibrium condition of $(\partial V/\partial r)_{eq}$ we obtain:

$$\Delta r=r-r_0=\{\frac{2r^2}{(r-r_0)}\}\{[\frac{(R-r-r_0^*)(R-r+r_0^*)}{2(R-r)^2}]-[\frac{1}{4(b-m/2R)}]$$
$$[\frac{n^*(R-r-r_0^*)^2(R-r+r_0^*)^2}{2(R-r)^4}-\frac{2r_0^2}{(R-r)^3}]\}\frac{\exp(-n^*(R-r-r_0^*)^2/2(R-r))}{\exp(-n(r-r_0)^2/2r)} \qquad (5)$$

From the condition of $(\partial^2/\partial r^2)=K_H$ and the assumption that

$K_0=4\pi^2\mu\omega^2c^2$ and $K_H=4\pi^2\mu\omega_H{}^2c^2$, we have:

$$\frac{\omega_H}{\omega}=\{(\frac{r_0}{r^3})(r_0^2-\frac{n(r-r_0)^2(r+r_0)^2}{4r})\exp(-n(r-r_0)^2/2r)+$$

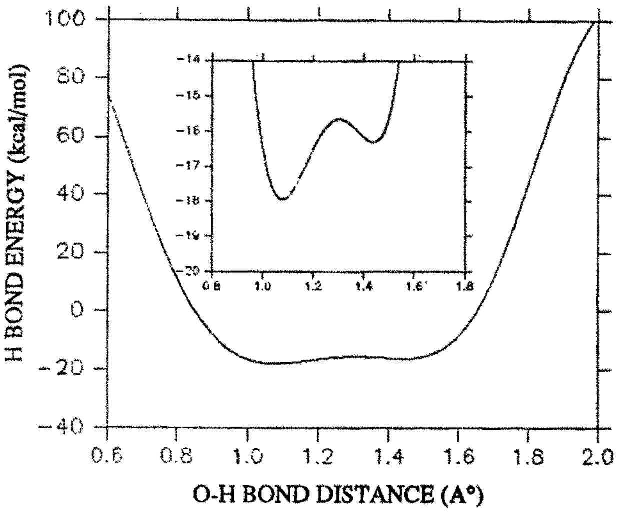

Figure 1. The potential energy curve for O...O distance of 2.45 Å [$n^*=13.32 \times 10^8 cm^{-1}$, m= 1 and $b=4.8 \times 10^8 cm^{-1}$]

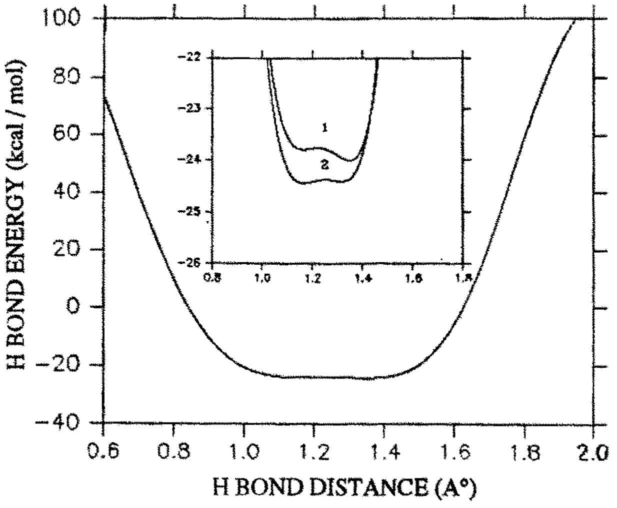

Figure 2. The potential energy curve for O...O distance of 2.4 Å [$n^*=13.32 \times 10^8 cm^{-1}$ and m=1]
(1) $b=4.8 \times 10^8 cm^{-1}$
(2) $b=5.0 \times 10^8 cm^{-1}$

$$\frac{r_0^*}{(R-r)^3}[r_0^{*}2-\frac{n^*(R-r-r_0^*)^2(R-r+r_0^*)^2}{4(R-r)}]$$

$$\exp(-n^*(R-r-r_0^*)^2/2(R-r))+[\frac{r_0}{4(b-m/2R)}]$$

$$[\frac{n^{*2}(R-r-r_0^*)^3(R-r+r_0^*)^3}{4(R-r)^6}-\frac{3n^*r_0^{*2}(R-r-r_0^*)(R-r+r_0^*)}{(R-r)^5}$$

$$\frac{6r_0^2}{(R-r)^4}]\exp[-n^*(R-r-r_0^*)^2/2(R-r)]\}^{\frac{1}{2}} \qquad (6)$$

Now from equations 3,5 and 6 it is possible to adjust n^*, m and b for a given molecule from experimental data such as hydrogen bond energies, structural parameters and OH stretching frequencies.

At this point, only for the purpose of comparison of the results obtained from equations 5 and 6 with the result of Lippincott and Schroeder, we will use the same parameters used by these authors:

$D = 118$ kcal/mole
$b = 4.8 \times 10^8 cm^{-1}$
$r_0 = r_0^* = 0.97 \times 10^{-8}$ cm
$n = k.r./D = 9.18 \times 10^8 cm^{-1}$
$n^* = 1.45n = 13.32 \times 10^8 cm^{-1}$
$nD = n^*D^*$
$m = 1$

The calculated O-H bond distances for a given R. fron equation 5 by method of successive approximation or fron the minimum in the plot of potential energy (equation 3 versus r for a set of repulsion constant b are given in Table along with the result of Lippincott and Schroeder. Th corresponding calculated frequencies with respect to un bounded OH stretching frequency of 3700 cm^{-1} are given i Table 2 and corresponding hydrogen bond energies ar given in Table 3.

Examination of Table 1 shows that although for 0- distance of 2.40 Å the O-H distance is not very sensitive t the value of b, for O-O distances greater than 2.40 Å O-I bond distance is sensitive to the value of b. As b increases, th O-H distance also increases. The dependence of O-H bon distance on b diminishes for large O-O bond distances. Th calculated OH stretching frequency and the hydrogen bon energy are also very sensitive to the value of b especially fc short hydrogen bonds. For a given O-O distance as b ir

Table 1. Calculated O-H distance for different O...O distances at different values b. (Distances are in Å)

O...O	Calculated OH bond distance^a							
2.40	1.163	1.164	1.165	1.165	1.165	1.165	1.165	1.165
2.45	1.151	1.079	1.081	1.088	1.094	1.098	1.100	1.010
2.50	1.115	1.046	1.048	1.053	1.057	1.061	1.064	1.067
2.55	1.079	1.029	1.027	1.039	1.034	1.037	1.040	1.041
2.60	1.051	1.011	1.013	1.016	1.018	1.020	1.022	1.024
2.70	1.019	0.994	0.994	0.996	0.998	0.999	1.000	1.001
2.80	0.998	0.984	0.984	0.986	0.986	0.987	0.988	0.989
2.90	0.986	0.978	0.978	0.979	0.980	0.980	0.981	0.981
3.00	0.980	0.975	0.975	0.975	0.975	0.976	0.976	0.976

a) O-H bond distances (calculated) in second column are from Reference 2, and O-H bond distances in columns 3-9 are calculated from equation 5 for b values of (4.8, 5.0, 5.5, 6.0, 6.5, 7.0 and 7.50 x10^8 cm^{-1} respectively).

Table 2. Calculated O-H stretching frequencies for different O...O distances at different values b. (Distances are in Å and frequences are in cm^{-1})

O...O	Calculated OH stretching frequencies^a							
2.40	2190	1060	1231	1273	1378	1461	1529	1585
2.45	1800	2109	2094	2030	1978	1950	1945	1891
2.50	1910	2584	2562	2508	2465	2422	2391	2359
2.55	2255	2806	2863	2732	2781	2746	2711	2698
2.60	2590	3090	3063	3030	3004	2979	2955	2931
2.70	3020	3342	3338	3312	3289	3274	3260	3247
2.80	3300	3489	3486	3464	3458	3445	3433	3422
2.90	3460	3577	3574	3562	3551	3547	3537	3534
3.00	3550	3625	3623	3620	3610	3608	3606	3597

a) OH stretching frequencies in second column are from Reference 2, and OH stretching frequencies in columns 3-9 are calculated from equation 5 for b values of (4.8, 5.0, 5.5, 6.0, 6.5, 7.0 and 7.50 x10^8 cm^{-1} respectively).

creases the hydrogen bond energy becomes more negative.

According to the above findings, we, unlike Lippincott and Schroeder, believe that the constant b in van der Waals repulsion term $V_3 = Ae^{-bR}$ is not transferable to all hydrogen bond systems. This conclusion has a logical explanation since one cannot expect, for example, the repulsion between two oxygens in hydrogen salt of carboxylic acids with a negative charge on oxygens to be the same as the repulsion of two oxygens in carboxylic acid dimers at the same distance. Besides, for the parameters given in reference 2, equations 4 or 5 are not capable of reproducing the experimental structural parameters. For example, consider the hydrogen bond in $N_2H_5C_2O_4$ with O-O distance of 2.448 Å and O-H bond distance of 1.224 Å. Equation 4 predicts a bond distance of 1. 151 Å and equation 5 a bond distance of 1.081 Å with calculated frequencies of 2185 cm^{-1} from equation 6 and 1940 from equation 19 of reference 2 respectively. Now it's possible that in equation 5 the experimental values of O-O and O-H bond distance vary n* for a given value of b and m until a best fit is obtained. From these sets of m, n* and b and experimental values for OH stretching frequencies and hydrogen bond energy one can select the appropriate values for m, n* and b.

The sets of b and n* for m=1 and m=6 which give the O-H bond distance of 1.224 Å are summarized in Table 4. The sets identified by (#) produce a double minimum potential function instead of a broad single minimum potential function for this symmetric hydrogen bond and the energy of the second minimum is lower than the first one; thus are rejected. The calculated hydrogen bond energies and OH stretching frequencies for acceptable sets are given in Table 4 and they are within the experimental value of 850 cm^{-1} [12]. From experimental or equantum mechanical calculations one could select the appropriate parameters for this molecule.

Table 3. Calculated O-H bond energy for different O...O distances at different values b. (Distances are in Å and hydrogen bond energies are in kcal/mol.)

O...O	Calculated hydrogen bond energy[a]						
2.40	-24.0	-24.5	-25.8	-27.0	-27.9	-28.8	-29.4
2.45	-17.9	-18.5	-19.7	-20.7	-21.6	-22.4	-23.0
2.50	-13.7	-14.1	-15.1	-16.0	-16.7	-17.4	-17.9
2.55	-10.5	-10.8	-11.7	-12.4	-12.9	-13.5	-13.9
2.60	-8.0	-8.3	-9.0	-9.6	-10.0	-10.5	-10.8
2.70	-4.7	-4.9	-5.3	-5.7	-6.0	-6.3	-6.5
2.80	-2.7	-2.9	-3.1	-3.4	-3.6	-3.7	-3.8
2.90	-1.6	-1.7	-1.8	-1.9	-2.1	-2.2	-2.3
3.00	-1.0	-1.0	-1.0	-1.2	-1.2	-1.3	-1.3

a) O-H bond energies in columns 2-8 are calculated for b values of (4.8, 5.0, 5.5, 6.0, 6.5, 7.0 and 7.50 x10^8 cm^{-1} respectively).

Table 4. Calculated O-H stretching frequencies and hydrogen bond energies for $N_2H_5HC_2H_5$ for different sets of b, n* and m. O...O distance= 2.448 Å and OH bond angle= 1.224 Å[a]

	m= 1			m= 6		
b x 10^8 cm^{-1}	n* x 10^8 cm^{-1}	Energy kcal/mol	Frequency cm^{-1} [a]	n* x 10^8 cm^{-1}	Energy kcal/mol	Frequency cm^{-1}
4.8	11.59#	-	-	11.99#	-	-
5.0	11.53#	-	-	11.86#	-	-
5.5	11.40#	-	-	11.69#	-	-
6.0	11.28#	-	-	11.54#	-	-
6.5	11.18	-34.89	793	11.41#	-	-
7.0	11.08	-36.58	939	11.29#	-	-
7.5	10.99	-38.12	1049	11.18#	-	-
8.0	10.91	-39.46	1136	10.99#	-	-

a) Geometrical parameters are from Reference 13.

#) See the text.

References

1. Baker, A.W. *J. Chem. Phys.*, **22**, 1625, (1954).
2. Lippincott, E.R. and Schroeder, R. *J. Chem. Phys.*, **22**, 1099, (1955).
3. Schroeder, R. and Lippincott, E.R. *J. Phys. Chem.*, **61**, 921, (1957).
4. Reid, C. *J. Chem. Phys.*, **30**, 182, (1959).
5. Singh, T. and Wood, J.L. *Ibid.*, **50**, 4567, (1968).
6. Brickman, J., Licha, A. and Zimmerman, H. *Ber. Bunsenges. Phys. Chem.*, **75**, 1324, (1971).
7. Gou, Q.Q. and Zhao, J.Y. *J. Molec. Sci.*, **3**, 17, (1983).
8. Jia, Y.Q. *Spectrochimica Acta*, **19A**, 1015, (1993).
9. Purcell, K.F. and Drago, R.S. *J. Am. Chem. Soc.*, **89**, 2874, (1967).
10. Kasende, O. and Zeegers-Huyskens, Th. *J. Phys. Chem*, **88**, 2132, (1984).
11. Olympia, P.L. and Fung, B.M. *J. Chem. Phys.*, **51**, 2876, (1969).
12. Lindgren, J., De Villepin, J. and Novak, A. *Chem. Phys. Letters*, **3**, 84, (1969).
13. Schuster, P., Zundal, G. and Sandorfy, C. (ed.). Data from *The hydrogen bond*, N.H.O.C. Vol. 2, chapter 8, (1976).