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ONE-DIMENSIONAL TREATMENT OF HYDROGEN BOND PART 2

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Abstract

The potential function of Lippincott and Schroeder for linear hydrogen bond has been re-examined and extended to nonlinear hydrogen bond. The parameters originally introduced to the potential function by Lippincott and Schroeder have been determined from the structural parameters such as O...O distance O-H bond distance, H...O distance and HOO angle. The validity of harmonic oscillator approximation for calculation of OH stretching frequency from the second derivative of this semi-empirical potential function has been investigated.

Introduction

Recently, we re-investigated the Lippincott and Schroeder [1] potential function for one-dimensional model of hydrogen bond and showed that the O-H bond distance and OH stretching frequency depends on the repulsive van der Waals potential constant and the attractive electrostatic potential constant [2]. In this paper, we will extend this potential function to nonlinear hydrogen bond.

Model and Calculations

The argument for setting up the potential function is exactly the same as the one given by Lippincott and Schroeder [1] for linear hydrogen bond

$$V= D[1-\exp(-n(r-r_0)^2/2r)] -D^* [\exp(-n^* (R-r-r_0^*)^2/2(R-r))]$$

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

where b is the repulsion constant in van der Waals repulsion term and m is the exponent in the electrostatic term. These two terms were originally modified to one term by Lippincott and Schroeder, as shown in equation 1, in order to reduce the number of constants to be evaluated.

In order to modify equation 1 to include nonlinear hydrogen bond, we propose the following potential function:

$$V= D[1-\exp(-n(\alpha r-r)^2/2\alpha r)] -D^* [\exp(-n^* (R-\alpha r-r_0^*)^2/2(R-\alpha r))]$$

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

where $\alpha = \cos(\Theta)$, and Θ is the HOO angle. In one-dimensional treatment of this potential function we force the hydrogen to move in the direction of O-O line in $r\sin(\Theta)$ distance from it. This restriction has been introduced as a correction term for nonlinearity of the hydrogen bond.

From the first derivative of equation 1 with respect to r, the O-H bond distance and the equilibrium condition of $(\partial V/\partial r)_{eq} = 0$, we have:

Keywords: H bond energy; Hydrogen bond; Potential function

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

From the condition of $(\partial^2 V/\partial r^2) = K_H$

$$K_H = nD\left\{\left[\frac{1}{\alpha r^3}\right]\left[r_0^2 - \frac{n(\alpha r - r_0)^2(\alpha r + r_0)^2}{4\alpha r}\right]\left[\exp\left(-n(\alpha r - r_0)^2/2\alpha r\right)\right]\right.$$
$$+\left[\frac{\alpha^2}{(R - \alpha r)^3}\right]\left[r_0^2 - \frac{n^*(R - \alpha r - r_0^*)^2(R - \alpha r + r_0^*)^2}{4(R - \alpha r)}\right]$$
$$\left[\exp\left(-n^*(R - \alpha r - r_0^*)^2/2(R - \alpha r)\right)\right] + \left[\frac{r_0}{4(b - m/2R)}\right]$$
$$\left[\frac{n^{*2}(R - \alpha r - r_0^*)^3 (R - \alpha r + r_0^*)^3}{4(R - \alpha r)^6} - \right.$$
$$\left.\left.\frac{3n^{*2} r_0^{*2}(R - \alpha r - r_0^*)(R - r + r_0^*)}{(R - \alpha r)^5} - \frac{6r_0^{*2}}{(R - \alpha r)^4}\right]\right.$$
$$\left.\left[\exp\left(-n^*(R - \alpha r - r_0^*)^2/2(R - \alpha r)\right)\right]\right\}^{\frac{1}{2}} \qquad (4)$$

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:

$$\omega_H = \omega(K_H/K_0)^{\frac{1}{2}} \qquad (5)$$

By assigning the value of 3700 cm^{-1} to stretching frequency of free OH in the gas phase and recalling that $K_0 = nD/r_0$ [1], one can calculate the OH stretching frequency of H bonded O-H.

Results and Discussion

In order to calculate the potential function parameters (b, m and n*) from equation 3, for a given molecule, we fix the values of R, r and Θ obtained from neutron diffraction data and then for a selected value for r_0 (hence n) and arbitrary values for m and b vary n* until the two sides of equation 3 are equal. From the sets of m, b and n* which fit into equation 3, we choose the one that gives the H...O distance and HOO angle obtained from neutron diffraction data.

Lippincott and Schroeder chose the gas value of 0.97Å for r_0 in the vibrational ground state of the water (0.974 Å) in their treatment of linear and nonlinear hydrogen bonds and hence the value of 9.18×10^8 for n [2,3]. This value is much larger than the vibration-less equilibrium value of 0.9572 Å for O-H bond distance of water in the gas phase reported by Benedict *et al.* [4]. Since the O-H bond distance obtained from neutron diffraction are equilibrium values it seems more appropriate to use this value in equation 3. For intermolecular hydrogen bonds involving hydrates, we are not able to find a reasonable set of n*, b and m for $r_0 = 0.97$ Å that fits into equation 3. For those hydrates whose OH bond distance is greater than 0.974 Å with $r_0 = 0.957$ Å (hence $n = 9.057 \times 10^8\ cm^{-1}$) we are able to find a set of n*, b and m which satisfies the requirement set above. It should be mentioned here that we should have used corrected geometries for thermal motion in these calculations instead of uncorrected geometries. For hydrates the correction for thermal motion is rather large because of the small moment of inertia of water molecule which introduces distortion into the geometry [5]. Since the correction term for O-H bond distance varies according to different models and they are not available for H...O distance and bond angles, we arbitrarily select the correction factor of .015 Å for O-H bond distance in intermolecular hydrogen bond of α-$(COOH)_2.2H_2O$.

Table 1 summarizes the calculated values of n*, b and m for some selected molecules. The calculated hydrogen bond energy for the first minimum, height of the barrier, the calculated OH stretching frequency from equation 5 and experimental frequencies for compounds of Table 1 are summarized in Table 2.

For symmetrical hydrogen bonds such as $N_2H_5HC_2O_4$ (linear) and KH succinate (nonlinear) there exist several sets of b and n* which fit into equation 3 with different H bond energies and OH stretching frequencies. Since experimental H bond energies are not available for intramolecular hydrogen bond and, as we will show below, the validity of harmonic oscillator assumption for calculation of O-H stretching frequency (equation 5) for symmetric hydrogen bonds is questionable, we are not able to select the potential parameters for these molecules.

For unsymmetrical hydrogen bonds there exists only one set of b and n* that fits into equation 3 and reproduces the other geometrical parameters such as H...O and H-O...O angle.

The calculated frequencies depend on the assumption of harmonic behavior near the bottom of the potential well. As is shown in Figure 1 for the case of $N_2H_5HC_2O_4$, the harmonic oscillator potential function for symmetrical O-H bond with K_H calculated from equation 4 matches the calculated potential function from the geometrical parameters only at the bottom of the potential well. Although the calculated stretching frequencies for symmetric hydrogen bonds from equation 5 (harmonic oscillator approximations) are within the range of experimental values, the validity of this approximation for calculation of OH stretching frequencies in this case is questionable. For asymmetric hydrogen bonds with low barriers between two potential wells, the calculated OH

Table 1. Calculated potential parameters from geometrical parameters for some selected compounds. In all of these calculations m= 1.

Compounds	Geometrical Parameters					Potential Parameters	
	O...O	O-H	H...O	Θ^b_1	Θ^c_2	b ($x10^8$ cm^{-1})	n^a
KH succinate	2.444	1.227	1.227	5.35	5.35	8-20	10.38-9.70
$N_2H_5C_2O_4$	2.448	1.224	1.224	0.0	0.0	8-20	10.29-9.65
KH_2PO_4	2.477	1.066	1.415	1.3	0.9	6.29	12.16
α-oxalic acid. $2H_2O$							
intramolecular	2.506	1.026	1.480	0.41	0.29	6.286	13.46
intermolecular	2.864	0.964	1.917	8.72	4.38		
	2.864	0.978[d]	1.407	9.60	4.91	13.759	15.71
Acetic acid	2.631	1.011	1.642	9.31	3.79	8.368	13.35

(a) Data are extracted from Reference 9, distances are in angstrom and angles are in degrees.
(b) H-O...O angle
(c) H...O...O angle
(d) O-H bond distance arbitrary is corrected by 0.015 A for thermal motion. Other geometrical parameters are corrected accordingly, see the text.

Table 2. The calculated hydrogen bond energy, barrier height between two minima in double potential well and calculated OH stretching frequency with harmonic approximation

Compounds	H Bond Energy kcal/mol.	Barrier Height kcal/mol. (cm^{-1})		OH Stretching (cm^{-1})	
				calc.	exp.[a]
KH succinate	-40.50- -53.15	0.0	0.0	724-1550	850
$N_2H_5HC_2O_4$	-40.30 -53.06	0.0	0.0	625-1453	850
KH_2PO_4	-20.60	3.59	(1258)	2238	1380
α-oxalic acid. $2H_2O$					
intramolecular	-13.77	8.62	(3022)	2735	1900[b]
					1500
intermolecular	-1.32	48.74	(17437)	3565	3480
Acetic acid	-0.26	18.96	(6646)	3106	2875

(a) Data are from Reference 10.
(b) From Reference 11

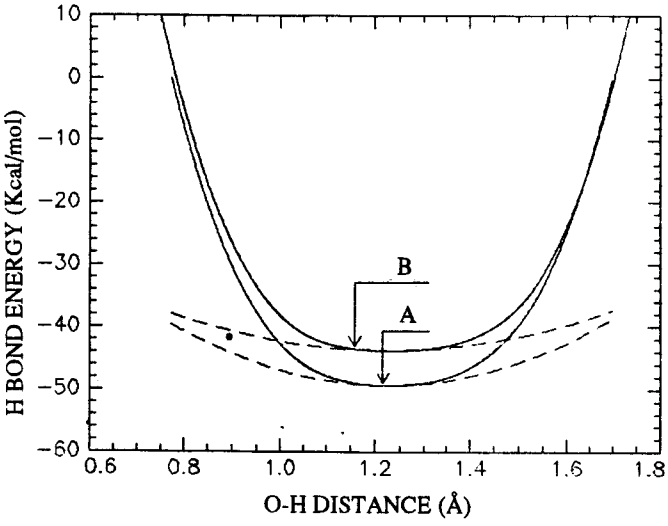

Figure 1. Semi-empirical potential function for $N_2H_5HC_2O_4$ (linear). Dotted curves represent the harmonic potentials with force constants calculated from the second derivative of the semi-empirical potential function.
(A) The potential curve for b =15.162 x 10^{-8} cm^{-1}.
n^*= 9.81 x 10^8 cm^{-1}.
(B) The potential curve for b = 10.172 x 10^8 cm^{-1},
n^*= 10.972 x 10^8 cm^{-1}.

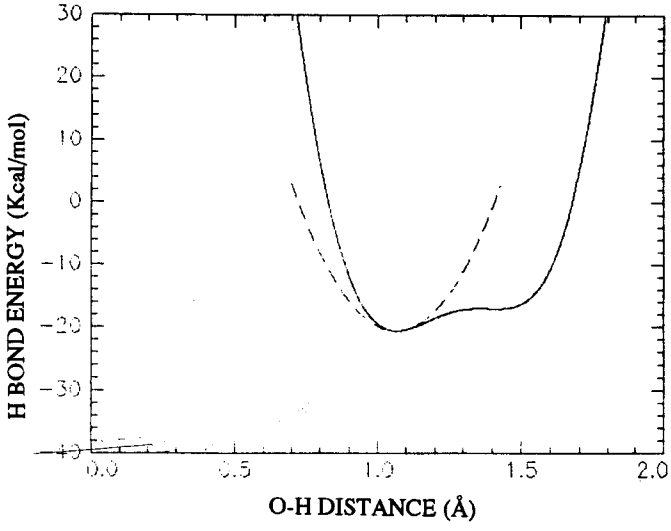

Figure 2. Semi-empirical potential function for KH_2PO_4. Dotted curve represents the harmonic potential with force constant calculated from the second derivative of the semi-empirical potential function.

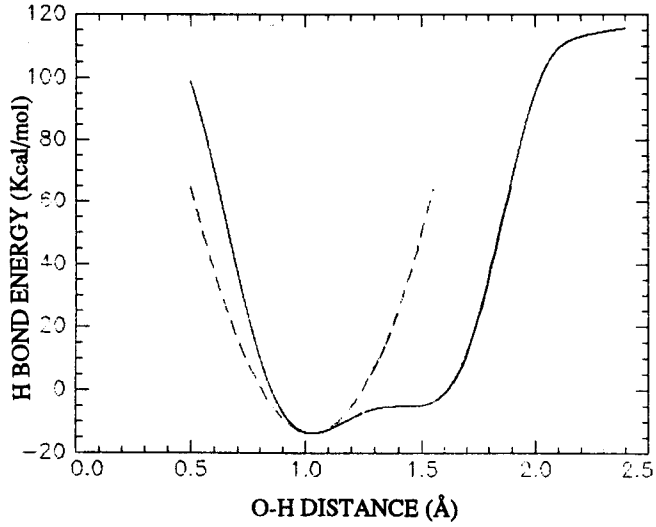

Figure 3. Semi-empirical potential function for intramolecular hydrogen bond in α-C_2O_4. $2H_2O$. Dotted curve represents the harmonic potential with force constant calculated from the second derivative of the semi-empirical potential function.

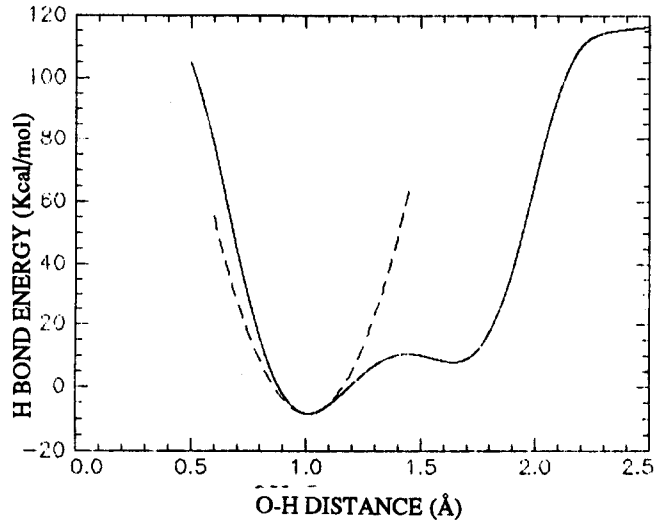

Figure 4. Semi-empirical potential function for intramolecular hydrogen bond in acetic acid (crystal). Dotted curve represents the harmonic potential with force constant calculated from the second derivative of the semi-empirical potential function.

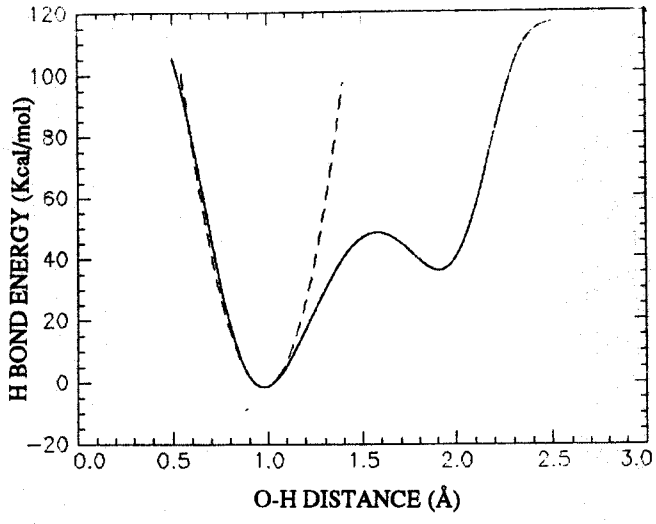

Figure 5. Semi-empirical potential function for intermolecular hydrogen bond in α-C_2O_4. $2H_2O$. Dotted curve represents the harmonic potential with force constant calculated from the second derivative of the semi-empirical potential function.

stretching frequency is much higher than the experimental values and this is due to the fact that the potential function is asymmetric (see Figs. 2 and 3 for the case of KH_2PO_4 and the intramolecular hydrogen bond in α-$(COOH)_2$. $2H_2O$). For the asymmetric hydrogen bond with a high barrier (CH_3COOH in solid state), as is apparent from the shape of potential function (Fig. 4), the assumption of harmonic oscillator is valid near the bottom of the potential well and hence the calculated OH stretching frequency is comparable with the experimental value (3106 cm^{-1} and 2875 cm^{-1} respectively). For the intermolecular hydrogen bond in α-$(COOH)_2$. $2H_2O$, the harmonic potential function almost fits into the first potential well of semi-empirical potential function (Fig. 5) and, as a result, the calculated OH stretching frequency of 3565 cm^{-1} is close enough to the experimental value 3480 cm^{-1}.

To conclude, it can be noted that the harmonic oscillator approximation for calculation of OH stretching frequency is not valid for the case of strong asymmetric hydrogen bonds and its validity for symmetric hydrogen bonds is questionable. For the strong asymmetric hydrogen bond as shown in Figures 2 and 3, the potential well is asymmetric and because of the low barrier between the two potential wells the first excited vibrational state lies near or above the top of the barrier. The symmetric hydrogen bond has a symmetric potential hole with a considerably flat bottom.

As our preliminary investigation shows, the semi-empirical potential function for symmetric hydrogen bond could be fitted to the Pöshl-Teller potential hole [6] and the first minimum of asymmetric hydrogen bond with low barrier to Morse type potential [7,8] which have standard solutions.

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