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The Use of the Lippincott/Schroeder Potential Function in Establishing Relationships between Infred Spectroscopic Measurements and Structural and Thermodynamic Properties of Hydrogen Bonds

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수소결합에 따른 적외선 분광기의 측정과 구조 및 열역학적 성질 사이의 관계식 성립에 관한 Lippincott/Schroeder 포텐샬 함수의 활용

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Abstract: A potential function is applied to a hydrogen bonded system such as O-H—O and is slightly modified to provide a good understanding of a range of data. The use of this model requires a knowledge of terms describing the Van der Waals repulsion and the electrostatic interaction and the determination of these terms from the equilibrium conditions is described. Using this simple model, it will be shown that the relationship between the frequency shift and enthalpy of hydrogen bond formation is predicted to be linear and this is in reasonable agreement with experimental results in the literature.

요 약: Lippin cott/Schroeder 포텐샬 함수는 OH···O와 같은 수소결합 시스템에 응용되고, 좋은 데이터를 주기 위하여 약간 수정된다. 이 모델의 사용은 Van der Waals 반발력과 정전기적 상호작용을 표현하는 항들을 요구하며, 이들 항들은 평형조건으로 부터 결정된다. 이 간단한 모델을 사용하므로서, 주파수이동과 수소결합 형성의 엔탈피 관계는 직선이 될 것으로 예상되며, 이것은 문헌에 있는 실험적 결과와 일치한다는 것을 보여준다.

1. Introduction

Hydrogen bonding has been a source of fascination to legions of physical chemists and physicists ever since the introduction of the concept in 1912 [1]. Although weak compared to covalent bonds, it is still an order of magnitude stronger than Van der Waals attraction. As a consequence, it play a key role in the structure of various liquids and solids and in the thermodynamics of mixing.

In low molecular weight materials, various aspects of hydrogen bonding can be directly studied, such as bond lengths, angles in crystalline structures, and the enthalpy of mixing, etc. In the case of polymers, however, this is not possible and such information can only be simulated or inferred. One

approach is to use various empirical correlations of infrared frequency shifts to structural parameters or thermodynamics quantities[2-7]. Such correlations are often not general, however, in that they vary in a non predictable manner between classes of materials. Clearly, it would be useful to make such correlations together using a theoretical model and we will attempt to do using the Lippincott-Schroeder potential function[8-10].

It will be shown that slight modifications to this model allow a good understanding of a range of data.

2. The Lippincott Potential Function

The potential function for a hydrogen bonded system, that was suggested by Lippincott and Schroeder[8-10] for a system such as O-H---O, provides a relationship between the O-H bond length, r, the O---O distance, R, and the vibrational frequency shift of the O-H band. Originally, this potential functions was introduced as a diatomic internuclear potential function[11] and only subsequently applied to hydrogen bonded systems. The function for a specific bond is of the form :

$$V=D\{1-\exp(-n\triangle r^2/2r)\} \quad (1)$$

D is the bond dissociation energy

$\triangle r=r-r_0$

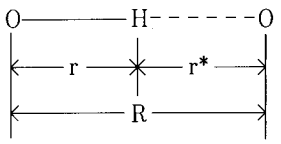
n is a parameter related to the ionization potentials of the atoms forming the bond and is equal to $k_0 r_0/D$, where r_0 is the unperturbed bond length(in this study, the bond length of the "free" or non hydrogen bonded group) and k_0 is the stretching force constant of unperturbed bond.

For a hydrogen bonded system such as that shown in Fig. 1, the Lippincott potential is written for each bond.

$$V_1=D\{1-\exp(-\alpha)\} \quad (2)$$

$$V_2=D^*\{1-\exp(-\beta)\}-D^* \quad (3)$$

(the factor D* is subtracted from V_2 so as to define V=0 at infinite separation).



r : OH BOND LENGTH OF H-BONDED GROUP
r* : HO BOND LENGTH OF H-BONDED GROUP
$\triangle r=r-r_0$
$r^* =R-r$

Fig. 1. Schematic linear model for a O-H---O hydrogen bond.

Also included are Van der Waals repulsion and electrostatic interaction terms between the oxygen and oxygen atoms.

$$V_3=Ae^{-bR} \quad (4)$$

$$V_4=-B/R^m \quad (5)$$

In equations (2) and (3), respectively

$\alpha=n(r-r_0)^2/2r$ and

$\beta=n^*(R-r-r_0^*)^2/2(R-r)$ (6)

(Lippincott assumed that in equation(5) m=1, Reid[12]later modified this to m=6, but the differences are minor).

Accordingly, the total potential can be written

$$V=V_1+V_2+V_3+V_4 \quad (7)$$

For O-H---O hydrogen bond systems, the sum of repulsion and electrostatic terms contain four parameters: A, B, b, and m.

$$V_3+V_4=Ae^{-bR}-B/R^m \quad (8)$$

The parameter B is eliminated by obtaining it in terms of A so that there are three instead of four constants. To do this it is possible to write.

$$V_3+V_4=V_0\{2\exp(-b(R-R_0)-3(R_0/R)^m\} \quad (9)$$

Where $-V_0$ is equal to(V_3+V_4) when $R=R_0$. By comparing equation (9) with equations (4) and (5) one can have

$$A=2V_0\exp(bR_0) \quad (10)$$

$$B=3V_0R_0^m \quad (11)$$

By dividing equation (11) by equation (10) one can obtain

$$V_3+V_4=A[\exp(-bR)-(3R_0/2R)\exp(-bB_0)^m]. \quad (12)$$

Hence, the hydrogen bond potential function is

$$V=D\{1-\exp(-\alpha)\}-D^*\{\exp(-\beta)\}+ A\{\exp(-bR)-(3R_0/2R)\exp(-bR_0)^m\} \quad (13)$$

Before this hydrogen potential function can be applied to predict properties of hydrogen bond systems, it is necessary to evaluate a parameter g. The evaluation of g defined as

$$g=n^*/n \quad (14)$$

Where n* refers to the H-O hydrogen bond(see fig. 1). For symmetrical hydrogen bonds g=1 and for (the more usual) asymmetric case g depends upon the strength of the hydrogen bond. As the hydrogen bonds get stronger, g gets smaller. Correlations between spectroscopic and crystallographic data have been reviewed by Novak[13] and using these data the parameter g for the O-H---O system has been evaluated as part of this study. A value of g=1.65 works well for most hydrogen bonds found in polymers(see below).

Various parameters(including the relationship between r and R and energy and infrared frequency shift) can be determinded from the equilibrium conditions;

$$(\partial V/\partial r)eq=0 \quad (15)$$

$$(\partial V/\partial R)eq=0 \quad (16)$$

$$(\partial 2V/\partial r^2)eq=K_H \quad (17)$$

$$(\partial 2V/\partial R^2)eq=K_{O\text{---}O} \quad (18)$$

where K_H and $K_{O\text{---}O}$ are the force constant values.

3. Calculations and Discussions

The relationship between O-H bond distance and O---O distance can be predicted from the hydrogen bond potential function equation (13) and the first equilibrium condition equation(15).

$$r=\{[D^*n^*/Dn]\,[\exp(\alpha-\beta)]r^2[(R-r)^2-r_0^{*2}]/ [(R-r)^2(r+r_0)]\}+r_0 \quad (19)$$

Since R, r_0, and n are known from experimental data and we assume $r_0=r_0^*$ and $n=gn^*$, r is easily calculated as a function of R by the method successive approximations, as described in the papers of Lippincott and Schroeder[8-10]. The appropriate parameters for the O-H---O hydrogen bond system are listed in table 1. A plot of calculated O-H distance as a function of O---O distance for hydrogen bonds is shown in Fig. 2. The experimental data[13, 14] are also plotted is this figure for comparision.

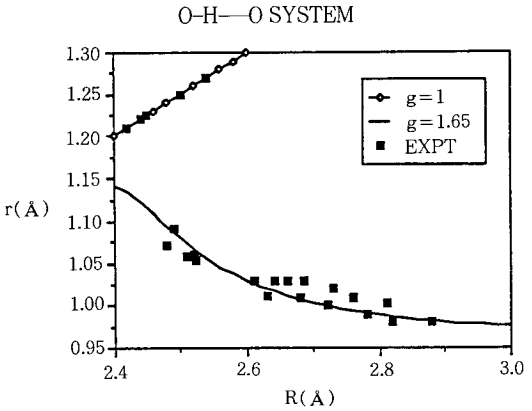


Fig. 2. Comparison of predicted and experimental O-H distance (r) as a function of O-----O distance (R) for O-H----O hydrogen bond.

Table 1. Parameters and Constants for Hydrogen Bond Systems of the Type of O-H---O

W(cm^{-1})	3611
K(dynes/cm)×10^5	7.2
K*(dynes/cm)×10^5	7.2
g(SYMMETRY)	1.
g(ASYMMETRY)	1.65
n(cm^{-1})×10^8	9.08
n*(cm^{-1})×10^8	14.9
r_0(Å)	0.97
r^*_0(Å)	0.97
D(Kcal/mole)	111.14
D*(Kcal/mole)	67.36
b(cm^{-1})×10^8	5.45
m	1

The experimental data falls into two classes, the first corresponding to "strong", hence short

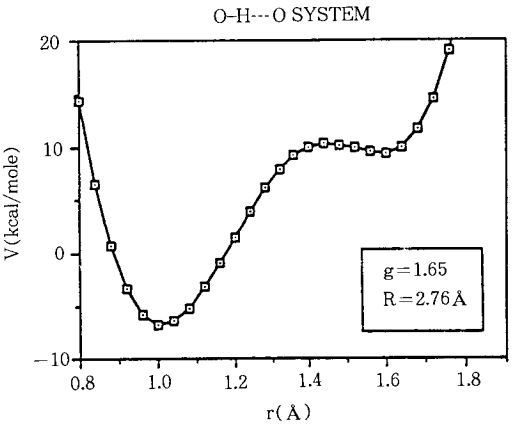


Fig. 3. Calculated O-H---O hydrogen bond potential curve for motion of proton along O----O axis for one fixed value of O---O distance(R=2.76Å).

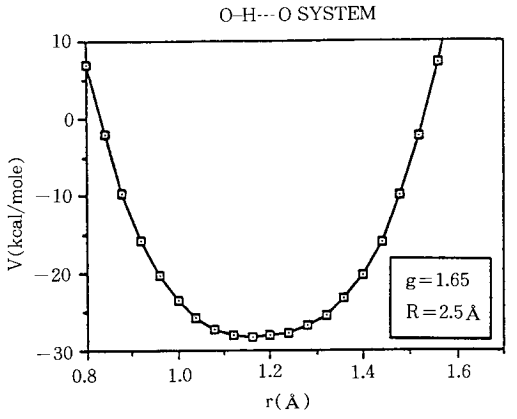


Fig. 4. Calculated O-H---O hydrogen bond potential curve for motion of proton along O----O axis for one fixed value of O---O distance(R=2.5Å).

hydrogen bonds, and the second is intermediate and weak(or longer) hydrogen bonds. Both are in excellent agreement with equation(19) providing that a value of g=1 is used for the former and g=1.65 for the latter.

Since the Lippincott model describes a number of properties associated with hydrogen bonding, we can also obtain potential curves for the motion of the hydrogen atom. To do so we have to evaluate

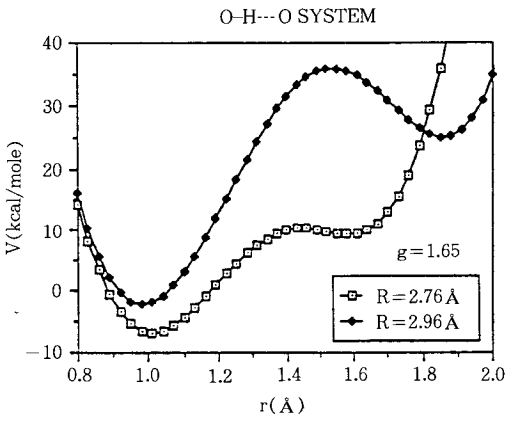


Fig. 5. Calculated O-H---O hydrogen bond potential curve for motion of proton along O----O axis for one fixed value of O---O distance(R=2.76Å, R=2.96Å).

the parameter A in the hydrogen bond potential by applying the equilibrium condition given by equation (16).

$$A=(n^*D^*/2)\,[1-(r_0^*(R-r))^2]\times[\exp(-\beta)]/[\exp(-bR)(b-3/2R)] \quad (20)$$

The potential curves can be calcuated as a function of O-H distance, r by using equation(13). These curves are shown in Fig. 3 and Fig. 4 for R=2.76Å and R=2.5Å, respectively. In the curves for motion of the H atom, Fig. 3 shows a double potential minimum while Fig. 4 shows single potential minimum. The second potential minimum in R=2.76Å lies nearly 10kcal/mole above the first minimum. As Lippincott and Schroeder mentioned[8, 9], these curves indicate that there should be considerable anharmonicity associated with the bonded OH frequency. Fig. 5 shows the O-H potential energy curves for different strength hydrogen bonds in O-H——O bond system. These curves illustrate the decrease in the potential barrier as the strength of the hydrogen bond increases.

The hydrogen bond potential function(equation (13)) can be also used to calculate the hydrogen bond energy, h_B. Fig. 6 shows a plot of h_B as a function of R. As R is increased hydrogen bond energy is decreased, as expected. Unfortunately, at present

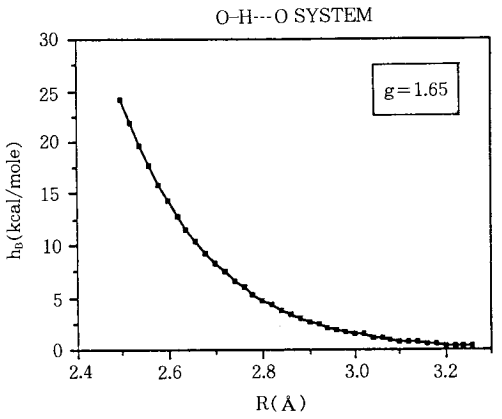


Fig. 6. Calculated relation between O---O distance (R) and hydrogen bond energy(h_B).

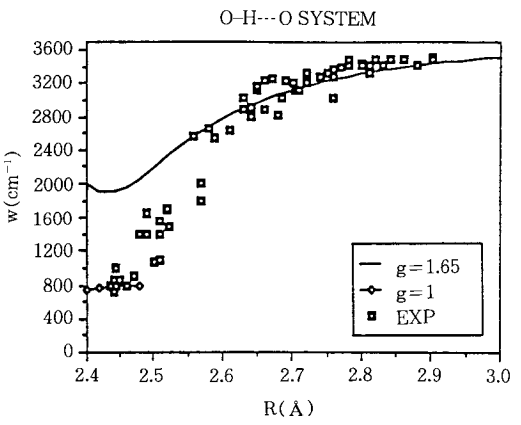


Fig. 7. Comparison of predicted and experimental OH bonded frequencies(W) as a function of O---O distance(R) for O-H---O hydrogen bond.

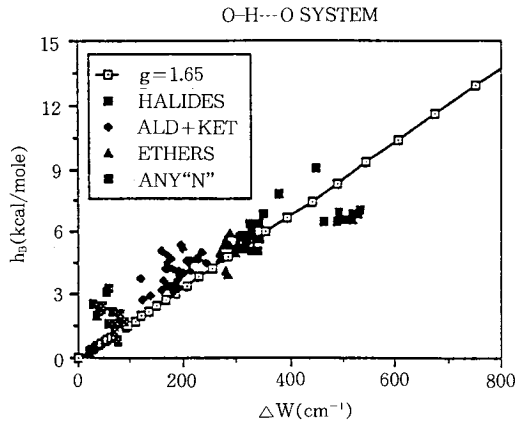


Fig. 8. Comparison of predicted and experimental OH frequency shifts(△W) as a function of enthalpy of hydrogen bond formation(h_B) for O-H---O hydrogen bond.

experimental data relating R to h_B is not available. However, the enthalpy(or energy) of hydrogen bond can be related to OH frequency shifts.

One of the most characteristic properties of the hydrogen bond is the relatively large frequency shift associated with the OH stretching mode of vibration. Through application of equation (13) and the third equilibrium condition equation (17) one obtains K_H, the force constant characteristic of this vibration.

$$K_H=(nD/r^3)[\exp(-\alpha)]\times[r_0^2-(n\triangle r^2/4r)(r+r_0)]+[n^*D^*/(R-r)^3]\times[\exp(-\beta)]\times[r_0^{*2}-n^*(R-r-r_0^*)^2(R-r+r_0^*)^2/4(R-r)] \quad (21)$$

The observed frequency of the hydrogen bonded band, relative to the unperturbed or "free" frequency, can then be determined from

$$W_H/W_0=(K_H/K_0)^{1/2} \quad (22)$$

and

$$W_0=\frac{1}{2\Pi C}\sqrt{\frac{K_0}{\mu}} \quad (23)$$

where C is the velocity of light and μ is the reduced mass of the atoms involved. We took 3611cm^{-1} as the frequency of the unbonded(free) OH stretching mode. Fig. 7 shows a plot of calculated hydrogen bonded O-H stretching frequency as a function of O——O distance for various hydrogen bonds. The experimental data[13] are also plotted in this figure for comparision. The agreement between experimental and predicted values is satisfactory for weak, [e. g. amides, urethanes, and OH's] to intermediate, [e. g. acids] hydrogen bonds. Also it is good for strong hydrogen bonds where we know g=1. In between there is poor agreement. Clearly, molecules with these intermediate characteristics have to be modeled separately.

Finally, a plot of calculated O-H frequency shift (△W) as a function of enthalpy of hydrogen bond formation(h_B) is shown in Fig. 8. It can be seen that

Table 2. Calculated r, w and △W Values

R(Å)	r(Å)	W(cm^{-1})	△W(cm^{-1})
2.50	1.0793	2188.03	1422.97
2.52	1.0666	2322.35	1288.65
2.54	1.0556	2448.52	1162.48
2.56	1.0456	2568.81	1042.19
2.58	1.0371	2675.23	935.77
2.60	1.0297	2770.52	840.48
2.62	1.0230	2857.88	753.12
2.64	1.0173	2934.15	676.85
2.66	1.0120	3004.83	606.17
2.68	1.0075	3066.37	544.63
2.70	1.0036	3120.75	490.25
2.72	1.0000	3170.67	440.23
2.74	0.9968	3215.41	395.81
2.76	0.9940	3255.19	355.81
2.78	0.9914	3291.71	319.29
2.80	0.9890	3325.09	285.91
2.82	0.9870	3354.04	256.96
2.84	0.9853	3379.47	231.53
2.86	0.9837	3402.93	208.07
2.88	0.9822	3424.51	186.49
2.90	0.9810	3442.98	168.02
2.92	0.9797	3461.11	149.89
2.94	0.9787	3476.34	134.66
2.96	0.9778	3490.08	120.92
2.98	0.9770	3502.42	108.58
3.00	0.9761	3514.66	96.34
3.02	0.9758	3519.60	91.40
3.04	0.9750	3532.91	78.09
3.06	0.9743	3542.12	68.88
3.08	0.9739	3549.01	61.99
3.10	0.9735	3555.45	55.55
3.12	0.9731	3561.49	49.51
3.14	0.9728	3566.57	44.43
3.16	0.9725	3571.31	39.69
3.18	0.9722	3575.75	35.25
3.20	0.9720	3579.33	31.67
3.22	0.9717	3583.24	37.76
3.24	0.9715	2586.34	34.66
3.26	0.9713	3589.24	21.76

Table 3. Calculated V_1, V_2, V_3, V_4 and h_B(kcal/mole)

R(Å)	V_1	V_2	V_3	V_4	h_B
2.50	5.45	−23.07	19.03	−28.54	−24.20
2.52	4.33	−20.19	17.28	−25.93	−21.84
2.54	3.45	−17.71	15.65	−23.47	−19.68
2.56	2.72	−15.54	14.12	−21.18	−17.70
2.58	2.17	−13.68	12.73	−19.10	−15.92
2.60	1.73	−12.07	11.47	−17.21	−14.30
2.62	1.38	−10.65	10.32	−15.49	−12.84
2.64	1.10	−9.42	9.29	−13.94	−11.53
2.66	0.88	−8.33	8.35	−12.52	−10.34
2.68	0.70	−7.38	7.51	−11.26	−9.28
2.70	0.57	−6.55	6.75	−10.12	−8.32
2.72	0.45	−5.81	6.06	−9.09	−7.45
2.74	0.36	−5.16	5.44	−8.16	−6.68
2.76	0.29	−4.58	4.88	−7.33	−5.98
2.78	0.23	−4.07	4.38	−6.57	−5.34
2.80	0.18	−3.61	3.92	−5.89	−4.78
2.82	0.15	−3.21	3.52	−5.28	−4.28
2.84	0.12	−2.85	3.15	−4.73	−3.82
2.86	0.10	−2.53	2.82	−4.24	−3.42
2.88	0.08	−2.25	2.53	−3.79	−3.05
2.90	0.06	−2.00	2.26	−3.39	−2.72
2.92	0.05	−1.78	2.02	−3.03	−2.43
2.94	0.04	−1.58	1.81	−2.71	−2.16
2.96	0.03	−1.40	1.61	−2.42	−1.93
2.98	0.03	−1.24	1.44	−2.16	−1.72
3.00	0.02	−1.10	1.29	−1.93	−1.53
3.02	0.02	−1.04	1.21	−1.82	−1.44
3.04	0.01	−0.87	1.02	−1.54	−1.21
3.06	0.01	−0.77	0.91	−1.37	−1.08
3.08	0.01	−0.68	0.81	−1.22	−0.96
3.10	0.01	−0.60	0.72	−1.08	−0.85
3.12	0.00	−0.54	0.64	−0.96	−0.75
3.14	0.00	−0.47	0.57	−0.86	−0.67
3.16	0.00	−0.42	0.51	−0.76	−0.59
3.18	0.00	−0.37	0.45	−0.68	−0.53
3.20	0.00	−0.33	0.40	−0.60	−0.47
3.22	0.00	−0.29	0.36	−0.53	−0.41
3.24	0.00	−0.26	0.32	−0.47	−0.37
3.26	0.00	−0.23	0.28	−0.42	−0.32

the relationship between the frequency shift and enthalpy of hydrogen bond formation is predicted to be linear, and this is in reasonable agreement with experimental results [15], given the degree of scatter in the reported data. This plot can be used to estimate h_B in O-H---O systems where these factors cannot be determined by the van't Hoff method.

Finally, for completeness, we tabulated the calculated values of r, $\triangle W$ and V_1, V_2, V_3, V_4, h_B for given values of R in table 2 and 3, respectively.

4. Conclusions

This simple Lippincott potential model of hydrogen bonded system such as O-H---O provides a link between OH frequency shift and OH bond length. Even better, the hydrogen bond energy can be related O-----O distance and O-H frequency shift. As already mentioned aboved, a plot of calculated O-H frequency shift($\triangle W$) as a function of enthalpy of hydrogen bond formation(h_B) is in reasonable agreement with experimental results in the reported data. This plot can be used to estimate h_B in O-H---O systems where these factors cannot be determined by the van't Hoff method.

Again, although this model has a limitation in some range, it gives very good information in understanding the nature of hydrogen bond.

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