

A SEMI EMPIRIC APPROACH TO COMPUTE THE DISSOCIATION ENERGY OF HYDROGEN BOUND TO SMALL MOLECULES OF CHEMICAL AND BIOLOGICAL INTEREST

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A Harrison method for covalent solids is extended and adjusted to calculate, semi empirically, the dissociation energy of hydrogen bound to small molecules of chemical and biological interest.

1. INTRODUCTION

At present, it is generally accepted the role of molecular physics to understand the chemical and biological phenomena. There seems to be little doubt that many of the fundamental biochemical processes in the living systems are directly connected with the properties of electrons and protons (hydrogen atoms) which obey the laws of quantum physics, quantum chemistry and molecular or quantum biology. Both in chemistry and biology we have to do with chemical reactions in which some molecules (as reactants) are dissociated giving rise to new molecules (as products).

In the process of forming and/or dissociating molecules one of the basic parameter is the cohesive (dissociation) energy required to separate the molecules into isolated atoms. The dissociation energy (also called cohesive energy or bond strength) can be calculated in different ways. But, no matter which way is used, it is necessary to take into account, quantum mechanically, the kinetic energy of electrons and nuclei of molecules, the electron-electron interaction (Coulomb, exchange and correlations), Coulomb interaction between nuclei and so called overlap energy. On the other hand it is well known that there is biological specificity for most of the bio-molecules. Because of this, in the study of cohesive energy for some specific atoms, very often, we can limit the calculations to a very small region (one atom or a small molecule) and to partition the system in inner and outer parts. The outer part may be taken into account in a simplified manner.

The aim of this paper is to propose a semi-empiric method to calculate the dissociation (cohesive) energy of hydrogen atoms bound (covalently) to small molecules of high interest in chemistry and biology.

2. THE THEORETICAL METHOD

In order to calculate the dissociation energy (the bound dissociation or bound strength) of hydrogen atoms bound to small molecules, in the following, we consider, as an appropriate extension, the approximation method used by W. A. Harrison for covalent molecules and solids with sp^3 hybridization [1, 2], in which we shall introduce some modifications.

The Harrison approximation is

$$E_{coh} = E_{bond} - E_{pro} - V_0(d) \quad (1)$$

where E_{coh} is the cohesive (dissociation) energy, E_{bond} is the energy gained in forming molecule, called bond formation energy, E_{pro} is the promotion energy obtained as the difference between hybrid energy per atom and the electron energy of the free atom, $V_0(d)$ is so called overlap energy containing contributions from kinetic, Coulomb and exchange energies – and d is the bond length. Further E_{bond} and E_{pro} are given by:

$$E_{bond} = 2\sqrt{V_{2h}^2 + V_{3h}^2} - \frac{\Delta z}{2} V_{3h} \quad (2)$$

$$E_{pro} = \left(1 + \frac{\Delta z}{4}\right) V_1^c + \left(1 - \frac{\Delta z}{4}\right) V_1^a \quad (3)$$

per bond and sp^3 hybridization;

$$E_{bond} = 2\sqrt{V_{2h}^2 + V_{3h}^2} - \frac{2\Delta z}{3} V_{3h} \quad (4)$$

$$E_{pro} = \left(1 + \frac{\Delta z}{3}\right) V_1^c + \left(1 - \frac{\Delta z}{3}\right) V_1^a \quad (5)$$

per bond and sp^2 hybridization;

$$E_{bond} = 2\sqrt{V_{2h}^2 + V_{3h}^2} - \Delta z V_{3h} \quad (6)$$

$$E_{pro} = \left(1 + \frac{\Delta z}{3}\right) V_1^c + \left(1 - \frac{\Delta z}{3}\right) V_1^a \quad (7)$$

per bond and sp hybridization.

In the above relations:

$$V_{2h} = \eta_h \frac{\hbar^2}{md^2} = 4.37 \frac{\hbar^2}{md^2} \quad (8)$$

is the Harrison's universal matrix element [1],

$$V_{3h} = \frac{\varepsilon_h^{(a)} - \varepsilon_h^{(c)}}{2} \quad (9)$$

$\varepsilon_h^{(a)}$ and $\varepsilon_h^{(c)}$ are the hybridization energies for the “anion” and “cation” respectively,

$$V_1 = \frac{\varepsilon_p - \varepsilon_s}{4} \quad (10)$$

is the metallic matrix element for the same atom, ε_p and ε_s being the Herman-Skillman terms and Δz is a charge difference depending of the electronic valence of involved atoms and of hybridization.

To assess the overlap energy $V_0(d)$ there are different ways. For example one can use Lennard-Jones potential or the procedures of [1–4].

Since our interest is to estimate the dissociation energy at the value of bond length that corresponds to the formation of molecule, instead of using one of the above-mentioned procedures, for reasons of simplicity, we replace E_{coh} from (1) by:

$$E_{Diss} = 2\sqrt{V_2^2 + V_{3h}^2} - \frac{\Delta z}{2}V_{3h} - E_{pro} \quad (11)$$

for sp^3 hybridization (also similar expressions for sp^2 and sp hybridization), where

$$V_2 = \eta_0 \frac{\hbar^2}{md^2} \quad (12)$$

The relation (11) is obtained if for $V_0(d)$ it is chosen the expression:

$$V_0(d) = 2\left[\sqrt{V_{2h}^2 + V_{3h}^2} - \sqrt{V_2^2 + V_{3h}^2}\right] \quad (13)$$

The parameter η_0 , which is different of Harrison universal parameter, absorbs most of the effects of E_{bond} and $V_0(d)$ and will be determined empirically. The other terms: V_{3h} , Δz , E_{pro} in (11) and (13) are the same as above and they can be calculated.

Our choice for E_{Diss} of (11) and $V_0(d)$ of (13), as it will be seen, is mainly supported by the agreement with experimental values for a group of molecules. Also from Harrison’s calculations it results that, for d at equilibrium, the kinetic and Coulomb plus exchange contributions to $V_0(d)$ are almost compensated for covalently bound molecules, which means that, approximately, around d (equilibrium) $V_0(d)$ could be considered as slowly varying with d . However, we have to draw the attention that because of stability reasons the relations (11) and

(13) could be good choices for molecules for which $\frac{V_{3h}^2}{V_2^2} \ll 1$. In that case, from the maximum of E_{Diss} it results $\eta_0 < 0$, but its value coming from the extremum of E_{Diss} leads to an underestimation of the dissociation energy.

3. THE RESULTS AND COMPARISON WITH THE EXPERIENCE

In order to calculate the dissociation energy from (11), first we have to determine the unknown parameter η_0 . As it has been mentioned, from the extremum of E_{Diss} , η_0 is negative. To get its numerical value we fit $E_{Diss}(calculated)$ with $E_{Diss}(experimental)$ for CH_4 molecule. The corresponding value is $\eta_0 \approx -0.485$ and does not depend on hybridization, which is an advantage.

Then, the same fitted value for CH_4 will be used to calculate E_{Diss} for quite a large numbers of molecules. The theoretical and experimental values are given in Table 1.

Table 1

Theoretical and experimental values of E_{Diss} in kilocalories *per mol and bond*

No	Molecule	$d(\text{\AA})$	$E_{Diss}(calc)$	$E_{Diss}(exp)$	Observations
1.	$\text{CH}_4 (sp^3)$	1.091	104.0	104.0 ± 1	Fitted value
2.	C_2H_6	1.107	100.1	98 ± 1	
3.	H_2O	0.958	116.1	119 ± 1	
4.	NH_3	1.008	100.6	110 ± 2	
5.	CH_3OH	1.096	102.6	94 ± 2	
6.	CH_3NH_2	1.093	103.35	94 ± 2	
7.	CH_3F	1.100	101.7	101 ± 2	
8.	CHF_3	1.098	102.7	106 ± 1	
9.	$\text{C}_2\text{H}_4\text{F}_2$	1.100	101.7	99 ± 1	
10.	CH_3Cl	1.110	99.4	100.9	
11.	CH_4S	1.104	100.8	> 88	
12.	SiH_4	1.480	104.4	94 ± 3	
13.	$(\text{CH}_3)_3\text{N}$	1.060	111.7	–	$E_{Diss}(exp.)$ no available
14.	COHOH	1.085	106.75	–	$E_{Diss}(exp.)$ no available
15.	SiH_3F	1.460	105.60	–	$E_{Diss}(exp.)$ no available
16.	SiH_3F	1.455	105.9	–	$E_{Diss}(exp.)$ no available

(continues)

Table 1 (continued)

No	Molecule	$d(\text{\AA})$	$E_{Diss}(calc)$	$E_{Diss}(exp)$	Observations
17.	CH ₃ CF ₃	1.084	107.0	106.7 ± 1	d from [6]
18.	C ₂ HOF ₃	1.090	105.5		d from [6]
19.	CH ₃ CH ₂ F	1.084	107.0	106.1*	* $E_{Diss}(calc.)$ ref. [6]
20.	C ₄ H ₁₀ - <i>t</i>	1.090	105.5	92 ± 1	d as the sum of covalent radii
21.	C ₃ H ₈ - <i>i</i>	1.090	105.5	95 ± 1	d as the sum of covalent radii
22.	(CH ₃) ₂ NH	1.090	105.5	95 ± 2	d as the sum of covalent radii
23.	C ₂ H ₅ OH	1.090	105.5	86 ± 0.8	d as the sum of covalent radii
24.	HNF ₂	1.060	86.4	75.7 ± 2.5	d as the sum of covalent radii
25.	C ₂ H ₄ (<i>sp</i> ²)	1.070	105.4	105 ± 0.4	
26.	CH ₂ O	1.060	108.2	87 ± 1	
27.	CH ₂ O	1.060	82.4	87 ± 1	If the metallicity is included
28.	C ₂ H ₄ O	1.090	98.7	86 ± 0.8	
29.	C ₂ H ₆ O	1.112	97.1	98.3 ± 1.8	d from [6]
30.	C ₂ F ₃ OH	1.090	100.2	91.0 ± 2	d from [6]
31.	C ₄ H ₆	1.086	101.2	–	d from [6] $E_{Diss}(exp.)$ no available

Since from the conditions of extremum of E_{Diss} or $V_0(d)$ the calculated values are systematically underestimated we believe the best way is to use for bond length d the experimental values. Most of d -values, together with $E_{Diss}(experimental)$, could be extracted from [5]. In other cases, since experimental values for d are not available we use for C₂H₅OH, (CH₃)₂NH, *i*-C₃H₈, HNF₂ the sum of covalent radii even if we expect the effect of other atoms to increase d , and for CH₃CF₃, C₂HOF₃, CH₃CH₂F the theoretical values of [6].

As it can be seen from Table 1 the agreement of theoretical values with the experimental ones is quite satisfactory. Also, for CH₃CF₃, CH₃CH₂F and C₂HOF₃ there is a good agreement with theoretical values of [6].

We have to note the trend of E_{Diss} with bond length d is in the right direction in most of the cases. As a matter of fact this was the motive that helped us in choosing the expression (11) for E_{Diss} .

In our calculations each molecule was considered as di-molecule, the effect of others atoms are absorbed in d and η_0 because it can be seen that $d(C-H)$ is varying very little from one to another molecule; in other words the outer part of the system has little contribution to E_{Diss} .

The metallicity of other atoms, forming the molecule is neglected. When this is taken into account in an approximate manner the tendency is to diminish E_{Diss} .

Even the above approach is a semi-empiric one, due to the agreement with experimental data, at least partially, we believe that the correct physics is included and this kind of calculation could be helpful when the dynamic flow of molecules through biological channels is studied. However it is necessary to be very careful in trying to generalize the method to more complex molecules since our approach can be better justified when $\frac{V_{3h}^2}{V_2^2} \ll 1$.

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