

### AB INITIO COMPUTATION OF FORCE CONSTANTS. III. A SIMPLE PROCEDURE FOR THE EVALUATION OF X–H BOND DISSOCIATION ENERGIES

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#### ABSTRACT

A simple expression derived from the Morse potential allows X–H bond dissociation energies to be estimated from the quadratic stretching force constants obtained in ab initio computations. Agreement with experiment is excellent for C–H bonds, except when the radical is stabilized by  $\pi$ -conjugative effects, in which case the bond dissociation energy is overestimated. The procedure also fails to estimate ionic dissociation energies.

#### INTRODUCTION

In Part II of this series [1] a method was proposed for the estimation of bond dissociation energies. This method is based upon an expression derived from the Morse curve and presumes the existence of an empirical relationship between the dissociation energy of a bond and the quadratic and cubic stretching force constants of this bond. The equation has the form  $D_e = A k_2^3/k_3^2$ , where  $k_2$  and  $k_3$  are the stretching force constants and A is a constant. When  $D_e$ ,  $k_2$  and  $k_3$  are expressed in units of kcal · mole<sup>-1</sup>, mdyn · Å<sup>-1</sup> and mdyn Å<sup>-2</sup> respectively, A is 648. Application of eqn. (1) to a number of second and third period hydrides provided calculated dissociation energies in good agreement with experiment. The force constants required for these calculations were obtained theoretically by the force method [2, 3] based on wavefunctions generated with the 4-31G basis set [4] of Gaussian 70 [5]. This programme provides computed quadratic and cubic stretching force constants that are in excellent agreement with experiment [6].

$$D_e \text{ (kcal mole}^{-1}\text{)} = 648 k_2^3/k_3^2 \quad (1)$$

## DISCUSSION

Subsequent to the submission of Part II of this series, sufficient additional data have become available to permit a more detailed evaluation of the applicability of eqn. (1) to systems containing X—H and, especially, C—H bonds. Column 5 of Table 1 summarizes the results. The  $r$  values listed in the first column of this Table correspond to  $R_e$  (experimental) rather than  $R_e$  (theoretical), because  $k_2$  and  $k_3$  are computed more accurately at these values [6].

The data presented in Table 1 indicate that reasonable estimates of bond dissociation energy can be obtained for several kinds of X—H bonds, agreement with experiment being best for C—H bonds. In addition, it is possible to compute quantities that are not at present susceptible to direct experimental measurement, for example, the non-equivalent C—H bonds of methanol, methylamine and methanethiol\*. In view of the simplicity of the procedure and the relatively minor computational effort that is involved, we believe that the success of the empirical relationship, eqn. (1), is remarkable. It is noteworthy that more complicated (and costly) ab initio computational schemes lead to bond dissociation energies that are in very poor agreement with experiment [1].

It is possible to simplify the procedure further by rewriting eqn. (1) so as to avoid the computation of  $k_3$ . Replacing this quantity with its truncated two term expansion leads to

$$D_e(\text{X—H}) = 648 \bar{k}_2^3 / (\bar{k}_3 + \bar{k}_4 \Delta r)^2 \quad (2)$$

in which  $\bar{k}_3$  and  $\bar{k}_4$  are average cubic and quartic force constants whose values depend only on X. For C—H bonds, values of  $\bar{k}_3$  and  $\bar{k}_4$  were determined, by a linear fit of  $k_3$  to  $\Delta r$  ( $\Delta r = \bar{r} - r$ ;  $\bar{r} = 1.093 \text{ \AA}$ ), to be  $32.22 \text{ mdyn} \cdot \text{\AA}^{-2}$  and  $220 \text{ mdyn} \cdot \text{\AA}^{-3}$ , respectively. For other bonds,  $\bar{r}$  and  $\bar{k}_3$  were chosen to be the values computed for the corresponding hydrides; these  $\bar{r}$  and  $\bar{k}_3$  values are shown in Table 1. For N—H, O—H and S—H bonds, the values of  $\bar{k}_4$  are 300, 400 and  $130 \text{ mdyn} \cdot \text{\AA}^{-3}$ , respectively. These can be refined when more data become available.

The computations of dissociation energies by the procedure of eqn. (2) are summarized in the sixth column of Table 1. The agreement with the dissociation energies obtained by use of eqn. (1) is excellent. Dissociation energies can therefore be estimated readily, by application of eqn. (2) to a calculated quadratic stretching force constant. This force constant is most commonly obtained by a three point energy computation followed by double numerical differentiation (all of the required data are already printed out in the widely used ab initio programme, Gaussian 70 [5]).

\*The conformational dependence of stretching force constants of C—H bonds adjacent to lone pairs is well-known [11]; however, the possibility that the dissociation energies of such bonds might also exhibit a conformational dependence has been discussed only briefly [7].

TABLE 1

Calculated<sup>a</sup> and experimental dissociation energies of X-H bonds<sup>b</sup>

Compound	$r^c$	Calculated Force Constants		Bond Dissociation Energy		
		$k_2$	$k_3$	eqn. (1)	eqn. (2)	Exp. <sup>d</sup>
<i>C-H bonds</i>						
1 H-CH <sub>3</sub>	1.093	5.488	-32.14	103.7	103.2	104.0
2 H-CH <sub>2</sub> NH <sub>2</sub> <i>anti</i> <sup>e</sup>	1.093	5.303	-32.06	94.0	93.1	94.1
	1.093	5.439	-32.22	100.4	100.4	
3 H-CH <sub>2</sub> OH <i>gauche</i> <sup>e</sup>	1.096	5.266	-31.49	95.4	95.0	95.5
	1.096	5.371	-31.66	100.2	100.8	
4 H-CH <sub>2</sub> SH <i>gauche</i> <sup>f</sup>	1.096	5.358	-31.78	98.7	100.1	
	1.096	5.426	-31.72	102.9	103.9	
5 H-CH <sub>2</sub> F	1.095	5.360	-31.72	99.2	98.8	≤ 102.8
6 H-CH <sub>2</sub> Cl	1.086	5.694	-33.81	104.6	104.9	100.9
7 H-CHCH <sub>2</sub> CH <sub>2</sub>	1.090	5.546	-32.80	102.7	102.2	100.4
8 H-CH <sub>2</sub> CH <sub>3</sub>	1.102	5.151	-30.53	95.0	96.8	98.0
9 H-CHCH <sub>2</sub>	1.086	5.805	-33.73	111.4	111.2	108.0
10 H-CCH	1.062	6.720	-38.61	131.9	129.0	128.0
11 H-CHO	1.090	5.470	-32.97	97.5	98.1	87.0
12 H-CHS	1.090	5.589	-33.56	100.4	104.6	
13 H-CN	1.066	6.566	-38.16	126.0	126.0	124.0
<i>N-H bonds</i>						
14 H <sub>2</sub> N-H	1.008	7.505	-49.17	113.3	113.3	104.1
15 CH <sub>3</sub> NH-H	1.014	7.141	-47.31	105.4	105.2	92.0
<i>O-H bonds</i>						
16 HO-H	0.957	8.707	-61.40	113.5	113.5	119.0
17 CH <sub>3</sub> O-H	0.960	8.391	-59.88	106.8	105.6	102.0
<i>S-H bonds</i>						
18 HS-H	1.355	3.903	-20.82	88.9	88.9	90.0
19 CH <sub>3</sub> S-H	1.333	4.368	-23.29	99.6	96.3	88.0

<sup>a</sup>Zero point vibrational effects have not been taken into account. <sup>b</sup>Units: bond lengths, Å; quadratic force constants, m dyn · Å<sup>-1</sup>; cubic force constants, m dyn · Å<sup>-2</sup>; bond dissociation energies, kcal · mole<sup>-1</sup>. <sup>c</sup>Bond lengths at which the force constants were computed. <sup>d</sup>Taken from refs. 7-10. <sup>e</sup>With respect to the NH<sub>2</sub> lone pair. <sup>f</sup>With respect to the OH(SH) bond.

However, it should be noted that quadratic force constants obtained in this manner contain a contaminating component of the quartic force constant [6]. To demonstrate this point, the energy is expanded in a Taylor series

$$E(r) = E(r_0) + [\partial E/\partial r]_{r_0} (r - r_0) + (1/2)k_2(r - r_0)^2 + (1/6)k_3(r - r_0)^3 + (1/24)k_4(r - r_0)^4 \quad (3)$$

If the force constant obtained by double numerical differentiation is denoted by  $k'_2$  then

$$k'_2 = (E(r_o + d) - 2E(r_o) + E(r_o - d)) d^{-2} = k_2 + (1/12)k_4d^2 \quad (4)$$

An estimate of the correct force constant,  $k_2$ , can be obtained by using the average value  $\bar{k}_4$  given above

$$k_2 = k'_2 - (1/12) \bar{k}_4d^2 \quad (5)$$

As the step size,  $d$ , in the numerical differentiation becomes smaller, the estimate of  $k_2$  improves ( $0.025 \leq d \leq 0.05$  and the use of an extended basis set is recommended). Equations (2) and (5) may be combined to yield a simple expression for the dissociation energy that requires only the computation of the energy at three points.

$$D_e = 648 (k'_2 - (1/12)\bar{k}_4d^2)^3 (\bar{k}_3 + \bar{k}_4 \Delta r)^{-2} \quad (6)$$

The resulting dissociation energies do not suffer significantly from those quoted in column 6 of Table 1.

Examination of the C-H bond dissociation energies (entries 1-13 of Table 1) indicates that the present method will overestimate this quantity when the moiety R is more stable as a radical than it is in the molecule R-H. This is especially noticeable in the case of H-CHO, for which the difference between the calculated and experimental values represents the stabilization energy of the formyl radical [7, 12, 13]. Our method also fails, at present, for bonds other than X-H, and it is not successful in the prediction of ionic dissociation energies. Whether these failures are caused by correlation effects, level crossing effects or resonance effects is not yet known. These problems are under investigation.

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