

## ***Ab Initio* Computation of Force Constants. II. The Estimation of Dissociation Energies from *ab initio* SCF Calculations**

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The dissociation energies of second and third period hydrides have been estimated by fitting a Morse potential to the harmonic and cubic stretching force constants computed from *ab initio* wavefunctions. The estimates thus obtained are superior to dissociation energies computed by direct differences of Hartree-Fock energies.

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On a estimé les énergies de dissociation des hydrides de la deuxième et de la troisième période en ajustant un potentiel de Morse aux potentiels de vibration harmonique et cubique calculés à l'aide de fonction d'ondes *ab initio*. Ces estimés sont supérieurs aux énergies de dissociation calculés par les différences directes des énergies de Hartree et Fock.

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The calculation of bond dissociation energies *ab initio* has proved to be a virtually intractable theoretical problem. Reasonable agreement with experiment has been achieved only in a relatively small number of cases because large and complicated wavefunctions that take electron correlation specifically into account must be employed. The purpose of this paper is to outline a method for the estimation of the dissociation energies of hydride bonds which requires only SCF wavefunctions computed with a moderate size basis set.

The general shapes of interatomic potentials are well known from studies of the band spectra of diatomic molecules (1). In favorable cases the R.K.R. method (2) allows the exact shape of the potential curve to be deduced directly from the vibrational spectrum. When the vibrational spectrum is insufficiently well known for the computation of an R.K.R. potential, it is possible to fit the experimental data to one of a number of empirical curves. The best known of these is the Morse function (3),

$$[1] \quad V(r) = D_e[1 - \exp(-\alpha(r - r_e))]^2$$

in which  $D_e$  is the dissociation energy and  $r_e$  is the

equilibrium bond length. The parameter  $\alpha$  is usually adjusted by fitting the potential  $V$  to the harmonic force constant  $k_2$ . A particular advantage of the Morse function is its ability to reproduce the cubic and quartic force constants,  $k_3$  and  $k_4$ . Thus, when the dissociation energy  $D_e$  is unobtainable or unreliable, the potential can be fitted to the observed cubic force constant by the use of [2a] and [2b].

$$[2a] \quad \left. \frac{\partial^2 V}{\partial r^2} \right|_{r_e} = k_2$$

$$[2b] \quad \left. \frac{\partial^3 V}{\partial r^3} \right|_{r_e} = k_3$$

In a recent study of the force fields of second and third period hydrides (4), it was found that harmonic and cubic stretching force constants computed by the force method (5) are in excellent agreement with experiment. This suggested that, as has been done experimentally, it might be possible to estimate dissociation energies by fitting a three-parameter potential to the bond length and the calculated harmonic and cubic force constants. A number of possible functions have been evaluated (6, 7). Those due to Morse eq. 1, Rydberg (2a) eq. 3, Varshni (6) eq. 4, and

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TABLE I. Estimated and experimental<sup>a</sup> dissociation energies<sup>b</sup>

Molecule	$r^c$	Computed force constants <sup>d</sup>			Dissociation energy, $D_e$						Hartree-Fock <sup>f</sup>
		$k_2$	$k_3$		[8a]	[9a]	[7]	[6]	Exp. <sup>e</sup>	SCF	
1 H <sub>2</sub>	0.7420	6.054	-38.88			90.4	84.5	95.1	104.2 <sup>g</sup>	80.5	83.9
2 HF	0.9170	9.874	-70.11		112.9	111.8	112.8	126.9	135.9	76.9	101.4
3 H <sub>2</sub> O	0.9568	8.707	-61.40		97.7	99.2	100.9	113.5	119.0	64.2	78.5
4 NH <sub>3</sub>	1.0080	7.505	-49.17		99.4	99.5	100.7	113.3	110.0	58.0	68.1
5 CH <sub>4</sub>	1.0930	5.488	-32.14		94.0	91.6	92.2	103.7	104.0	79.3	80.1
6 HCl	1.2744	5.183	-29.37		86.1	90.3	93.0	104.6	103.1	57.8	77.7
7 H <sub>2</sub> S	1.3552	3.903	-20.82		73.1	76.7	79.0	88.9	90.0	48.2	64.4
8 PH <sub>3</sub>	1.4332	2.994	-13.89		78.6	79.1	80.1	90.1	77.0	43.5	55.5
9 SiH <sub>4</sub>	1.4780	2.906	-12.50		93.0	90.1	90.5	101.8	94.0	61.3	63.3
10 CO	1.1280	21.739	-146.88	247.8	263.9	274.3	308.6	322.8	256.7	131.7	182.7
11 N <sub>2</sub>	1.0940	27.396	-191.56	291.2	310.4	322.8	363.1	363.1	226.8	61.4	121.6
12 F <sub>2</sub>	1.4350	7.425	-36.91	161.3	168.5	173.1	194.7	194.7	37.7	-45.5	-31.6

<sup>a</sup>Zero point vibrational effects have not been taken into account.<sup>b</sup>Bond lengths in Å; quadratic and cubic force constants in mdyne/Å and mdyne/Å<sup>2</sup>; dissociation energies in kcal/mol.<sup>c</sup>Bond length at which the force constants were computed (see ref. 4).<sup>d</sup>Force constant data for molecules 2-9 were computed in ref. 4; 1, 10-12 in the present work.<sup>e</sup>Reference 5.<sup>f</sup>Calculated from data presented in ref. 10 (compounds 1-5, 10-12) and ref. 11 (6-9).

Lippincott and co-worker (8) eq. 5 were considered to be the most suitable (7).

$$[3] \quad V(r) = D_e \left[ 1 - (1 + \beta(r - r_e)) \times \exp(-\beta(r - r_e)) \right]$$

$$[4] \quad V(r) = D_e \left[ 1 - \frac{r_e}{r} \exp(-\beta(r^2 - r_e^2)) \right]^2$$

$$[5] \quad V(r) = D_e \left[ (1 - \exp(-x)) \times (1 - ab\sqrt{x} \exp(-b\sqrt{xr/r_e})) \right]$$

$$b = 1.065$$

$$x = k_2 r_e (r - r_e)^2 / 2D_e r$$

For the Morse and Rydberg potentials the resulting expressions for dissociation energy have the simple form shown in [6] and [7].

$$[6] \quad D_e(\text{Morse}) = 9k_2^3 / 2k_3^2$$

$$[7] \quad D_e(\text{Rydberg}) = 4k_2^3 / k_3^2$$

For the Varshni potential, the dissociation energy is given by [8a].

$$[8a] \quad D_e(\text{Varshni}) = 2C^3 / (B^2 + 2BC - 3C^2 - (C + B)\sqrt{(C + B)^2 - 8C^2})$$

in which

$$[8b] \quad B = -k_3 r_e^3 / 6$$

$$[8c] \quad C = k_2 r_e^2 / 2$$

In the case of the Lippincott potential, the procedure of ref. 8 is adopted, *i.e.*,

$$[9a] \quad D_e(\text{Lippincott}) = (b^2/2)k_2 r_e^2 (1 - 5a/4)$$

in which

$$[9b] \quad a = F / (1 + 5F/4)$$

$$[9c] \quad F = B/C - 1$$

(*i.e.*  $F$  is defined as in ref. 6)

Table I summarizes the results. The computed  $k_2$  and  $k_3$  were used in [6]–[9] to estimate the dissociation energy. The Varshni function was not suitable for  $\text{H}_2$ . The experimental  $D_e$  refer to the process  $\text{XY} \rightarrow \text{X} + \text{Y}$  and  $\text{XH}_n \rightarrow \text{XH}_{n-1} + \text{H}$ . The calculated Hartree–Fock and SCF  $D_e$  were obtained from the difference between the energy of the molecule and the fragments computed either near the Hartree–Fock limit or at the same level as the force constant calculations. Since energies were in general not readily available for the dissociation fragments of the poly-

atomic hydride,  $D_e$  was estimated as  $(1/n)(\text{XH}_n \rightarrow n\text{H} + \text{X})$ .

If the complete range of molecules is examined, it is evident that the estimated and calculated  $D_e$ 's for  $\text{F}_2$  are very much in error, and these will not be considered further. The dissociation energies of the remaining molecules seem to be represented best by the Varshni function, [8], but closer examination reveals that the reason for this is the lower error in the non-hydride molecules. If only the hydrides are considered, the Morse function is clearly superior and it is evident that  $D_e$  computed with the Morse potential, [6], are much better than either the Hartree–Fock  $D_e$  or the SCF  $D_e$ .

It has thus been found that the dissociation energies of hydride bonds can be computed satisfactorily with moderate size SCF wavefunctions. The method is superior to the direct computation of dissociation energies in terms of energy differences. Application of the procedure to the study of the dependence of bond dissociation energies on molecular conformations and the effects of substituents on bond dissociation energies is in progress.

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