

Dissociation energies for the electronic ground states of BeCl, GaH and LiH

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Abstract. The dissociation energies of the diatomic molecules BeCl, GaH and LiH have been computed by fitting empirical potential functions to the true potential energy curves for the electronic ground states of the molecules. The Lippincott three-parameter potential function, the five-parameter Hulburt-Hirschfelder potential function and the Szöke and Baitz electronegativity potential function have been used. The estimated dissociation energies D_0^0 are 4.50, 3.09 and 2.94 eV for BeCl, GaH and LiH respectively. These values compare well with the experimental values.

Keywords. Dissociation energy; BeCl; GaH; LiH; modified Lippincott function; Hulburt-Hirschfelder potential function; Szöke and Baitz function; electronegativity function; curve fitting method.

1. Introduction

Dissociation energies of diatomic molecules are of great interest in thermochemistry, combustion physics, astrophysics and likewise. In quantitative problems of valency, statistical calculations of equilibria at high temperatures, in chemical bonding and in many other problems the dissociation energy plays a fundamental role. Spectroscopists and chemists are concerned with the determination of reliable values of dissociation energies for the diatomic molecules.

It is proposed here to estimate the dissociation energies of the molecules of BeCl, GaH and LiH. For these molecules many investigators have determined the values of dissociation energy by different methods (Huber and Herzberg 1979). It is found that these values differ.

In the case of BeCl molecule, the thermochemical value of dissociation energy D_0^0 is 4.51 eV (Farber and Srivastava 1974), the mass-spectrometric method gives 3.98 eV (Hildenbrand and Theard 1969); Carleer *et al* (1977) report a value of 3.45 eV by inverse predissociation method, and Gaydon (1968) suggests 3.0 eV. For GaH molecule, Kronekvist *et al* (1971) report that the dissociation energy D_0^0 is less than 2.84 eV by predissociation method, Neuhaus (1959) reports 2.92 eV and Ginter and Innes (1961) report 2.94 eV. Way and Stwalley (1973) report that D_0^0 value for LiH as 2.43 eV by fitting the predissociation data with the calculated long range potential. Since then the molecular constants for the ground state of LiH have been revised, the dissociation energy of LiH is estimated in the present work with the new data.

Curve fitting method has been found to yield reliable dissociation energies for a large number of diatomic molecules (Singh *et al* 1970). The procedure consists in fixing the empirical potential function which best fits the true potential energy curve for the electronic ground state of the molecule. Many empirical potential functions are known for the diatomic molecules. Of these, functions given by Lippincott *et al* (1961) in the modified form, by Hulburt and Hirschfelder (1941), and by Szöke and Baitz (1968) have been found to describe adequately the potential energies of many molecules. These functions are therefore adopted in the present work to estimate the dissociation energies of BeCl, GaH and LiH.

2. The empirical potential functions

The empirical potential functions used are given below.

(i) The three parameter Lippincott function in the modified form:

$$U(r) = 8068.3 D_e \left[1 - \exp \left\{ - \frac{n(r - r_e)^2}{2r} \right\} \right] \\ \times \left[1 - a \left(\frac{b^2 n}{2r} \right)^{1/2} (r - r_e) \exp \left\{ - \left(\frac{b^2 n}{2r_e} \right)^{1/2} (r - r_e) \right\} \right], \quad (1)$$

where $n = 2\Delta/r_e$, $a = 4/5 \left(1 - \frac{1}{b\Delta^{1/2}} \right)$, $b = 1.065$ and

$$\Delta = \frac{0.018378 \mu_A \omega_e^2 r_e^2}{D_e \times 10^{-12}}.$$

(ii) The five parameter Hulburt-Hirschfelder (H-H) function:

$$U(r) = 8068.3 D_e [(1 - e^{-x})^2 + cx^3 e^{-2x} (1 + bx)], \quad (2)$$

where $x = \frac{\omega_e (r - r_e)}{2(B_e 8068.3 D_e)^{1/2} r_e}$,

$$c = 1 + a_1 \left(\frac{8068.3 D_e}{a_0} \right)^{1/2},$$

$$b = 2 - \left[\frac{7}{12} - \left(\frac{8068.3 D_e a_2}{a_0} \right) \right] / c,$$

$$a_0 = \frac{\omega_e^2}{4B_e}, \quad a_1 = -1 - \left(\frac{a_e \omega_e}{6B_e^2} \right), \text{ and}$$

$$a_2 = \frac{5}{4} a_1^2 - \frac{2\omega_e x_e}{3B_e}.$$

(iii) The Szöke and Baitz electronegativity function :

$$U(r) = 8068.3 D_e \left[1 - \exp \left\{ -\frac{\gamma (r - r_e)^2}{2r} \right\} \right] \\ \times \left[1 - a \left(\frac{b^2 \gamma}{2r} \right)^{1/2} (r - r_e) \exp \left\{ -\left(\frac{b^2 \gamma}{2r_e} \right)^{1/2} (r - r_e) \right\} \right], \quad (3)$$

where
$$\gamma = \frac{de}{(1.60199 \times 10^{-12} D_e)^{1/2}}.$$

$$d = \frac{5.8883 \times 10^{-2} \mu_A \omega_e^2 r_e}{(e_1 e_2 1.60199 \times 10^{-12} D_e)^{1/2}}$$

$$a = 0.35 e^{1/2}, e = (e_1 e_2)^{1/2} \text{ and } b = 1.065.$$

Szöke and Baitz (1968) have constructed this electronegativity potential energy function by the aid of parameters other than spectroscopic constants to render the possibility of linking different areas in chemical physics and they have replaced the force constant k_e of diatomic molecule by an expression connected with Pauling (1960) electronegativities e_1, e_2 as

$$k_e = d(e_1 e_2 1.60199 \times 10^{-12} D_e)^{1/2} r_e^{-1}, \quad (4)$$

In these functions, $U(r)$ is the potential energy (in cm^{-1}) for the internuclear separation r (in cm) in terms of the spectroscopic constants of dissociation energy D_e (in eV); and in units of cm^{-1} , the vibrational frequency ω_e , the anharmonicity $\omega_e x_e$, the rotational constants, B_e, α_e , all corresponding to r_e , the equilibrium internuclear separation of the molecule.

3. Method of evaluating the dissociation energy

For the electronic ground state of the molecule, the true potential energy curve can be constructed from the experimental energy levels by the procedure of Vanderslice *et al* (1960) for the Rydberg-Klein-Rees (RKR) method. The curve is represented by r_{\min} and r_{\max} values for the observed vibrational levels. For these r values, the energies $U(r)$ are calculated with the empirical potential functions by varying the D_e value. An average percentage deviation is determined between the calculated $U(r)$ and the experimental $G(v)$ values. The dissociation energy from any function is that value of D_e which gives the least deviation. And the function leading to smallest deviation determines the dissociation energy of the molecule. The dissociation energy referred to $v = 0$ level is given by $D_0^o = D_e - G(0)$.

The molecular constants used in the present study are listed in table 1. The true potential energy curves for BeCl, GaH and LiH have been taken respectively from the works of Janardan Singh and Prabhuram (1975), Girtle and Battino (1965) and, Orth

Table 1. Molecular constants for the electronic ground states of BeCl, GaH and LiH.

Molecule		BeCl	GaH	LiH
Pauling (1960) Electro- negativities	e_1	1.5	1.8	1.0
	e_2	3.0	2.1	2.1
ω_e (cm ⁻¹)		847.19	1604.52	1406.24
$\omega_e x_e$ (cm ⁻¹)		5.14	28.77	23.5505
B_e (cm ⁻¹)		0.7285	6.137	7.5134
α_e (cm ⁻¹)		0.0069	0.181	0.21582
r_e (Å)		1.797	1.663	1.5957
Reference		Janardan Singh and Prabhuram 1975	Ginter and Innes 1961	Orth and Stwalley 1979

Table 2. Estimated dissociation energies of the electronic ground states of BeCl, GaH and LiH.

Molecule	BeCl	GaH	LiH
Modified Lippincott function	3.18	2.20	2.21
	0.84	5.51	3.52
Hulburt- Hirschfelder function	4.50	3.09	2.94
	0.74	4.58	0.26
Electronegativity function	2.85	2.30	2.31
	1.17	5.33	2.73

First row: D^0 in eV

Second row: Average percentage deviation.

Table 3. Energy values from the n - n function for BeCl.

v	RKR r (Å)	$G(v)$ (cm ⁻¹)	$U(r)$ in cm ⁻¹		
			$D_e=4.54$ eV	$D_e=4.55$ eV	$D_e=4.56$ eV
0	1.727	422.31	418.25	418.25	418.25
1	1.680	1259.22	1263.24	1263.24	1263.24
2	1.650	2085.85	2098.15	2098.14	2098.13
3	1.627	2902.20	2919.36	2919.33	2919.31
4	1.609	3708.27	3683.96	3683.92	3683.87
5	1.592	4629.295	4513.26	4513.19	4513.12
0	1.876	422.31	421.27	421.27	421.27
1	1.940	1259.22	1254.57	1254.58	1254.58
2	1.988	2085.85	2087.32	2087.34	2087.35
3	2.029	2902.20	2904.92	2904.96	2905.01
4	2.066	3708.27	3708.20	3708.29	3708.38
5	2.101	4629.295	4512.83	4512.97	4513.12
Average percentage deviation			0.7431	0.7430	0.7432

Table 4. Energy values from the H-H function for GaH.

v	RKR r (Å)	$G(v)$ (cm ⁻¹)	$U(r)$ in cm ⁻¹		
			$D_e=3.18$ eV	$D_e=3.19$ eV	$D_e=3.20$ eV
0	1.531	795.1	760.11	760.11	760.11
1	1.450	2343.3	2270.57	2270.55	2270.52
2	1.401	3837.1	3720.65	3720.57	3720.49
3	1.366	5278.8	5060.68	5060.52	5060.35
4	1.338	6670.6	6342.63	6342.35	6342.08
5	1.316	8014.5	7495.36	7494.96	7494.56
6	1.297	9312.7	8603.11	8602.56	8602.03
7	1.282	10567.5	9556.38	9555.69	9555.01
8	1.270	11780.9	10371.92	10371.09	10370.28
9	1.261	12955.1	11015.84	11014.90	11013.98
10	1.254	14092.3	11536.47	11535.43	11534.40
0	1.824	795.1	822.90	822.91	822.91
1	1.965	2343.3	2385.92	2385.98	2386.04
2	2.076	3837.1	3889.00	3889.23	3889.47
3	2.176	5278.8	5336.36	5336.93	5337.50
4	2.270	6670.6	6721.91	6723.02	6724.13
5	2.362	8014.5	8067.89	8069.79	8071.66
6	2.451	9312.7	9339.41	9342.33	9345.22
7	2.540	10567.5	10566.85	10571.08	10575.27
8	2.628	11780.9	11728.08	11733.87	11739.63
9	2.716	12955.1	12831.39	12839.04	12846.63
10	2.804	14092.3	13873.46	13883.21	13892.89
Average percentage deviation			4.5800	4.5796	4.5798

and Stwalley (1979). Table 2 displays the dissociation energies determined by different potential functions, and also the average percentage deviations. Only relevant results of $U(r)$ are given in tables 3, 4 and 5 for BeCl, GaH and LiH respectively. The calculations were carried out on the DCM MICRO SYSTEM 1101 in steps of 0.01 eV for values of D_e ranging from 1.5 to 6.0 eV for each molecule.

4. Conclusions

The Hulburt-Hirschfelder function leads to the dissociation energies of BeCl, GaH and LiH as the deviation is the least. For BeCl, the estimated dissociation energy of 4.50 ± 0.12 eV agrees with the thermochemical value of 4.51 eV (Farber and Srivastava 1974). We note that the Gaydon's (1968) value 3.0 eV is different from the experimental value. Experimental dissociation energy of GaH is found to be less than 2.84 eV by predissociation method (Kronekvist *et al* 1971). The estimated value of 3.09 ± 0.20 eV agrees within 9%, and also it is close to other reported values. The estimated dissociation energy for LiH is 2.94 ± 0.07 eV. Since the Hulburt-Hirschfelder function fits adequately the experimental data, this value can be considered as satisfactory.

The error indicated in the results takes into account the error of 2% inherent to

Table 5. Energy values from the H-H function for LiH.

v	RKR r (Å)	$G(v)$ (cm^{-2})	$U(r)$ in cm^{-1}		
			$D_e=3.02$ eV	$D_e=3.03$ eV	$D_e=3.04$ eV
0	1.4458	698.12	697.69	697.69	697.69
1	1.3532	2058.01	2056.98	2056.95	2056.93
2	1.2967	3372.78	3370.50	3370.43	3370.35
3	1.2548	4643.54	4636.92	4636.76	4636.60
4	1.2213	5871.27	5856.47	5856.21	5855.94
5	1.1934	7056.74	7029.42	7029.02	7028.63
6	1.1694	8200.60	8163.96	8163.41	8162.86
7	1.1486	9303.32	9248.92	9248.19	9247.47
8	1.1301	10365.19	10298.93	10298.00	10297.09
9	1.1136	11386.35	11307.18	11306.04	11304.92
10	1.0987	12366.78	12279.04	12277.69	12276.35
11	1.0851	13306.30	13219.51	13217.92	13216.36
12	1.0727	14204.55	14123.43	14121.60	14119.80
0	1.7780	698.12	696.84	696.84	696.85
1	1.9367	2058.01	2056.32	2056.37	2056.42
2	2.0607	3372.78	3369.81	3370.00	3370.20
3	2.1717	4643.54	4638.59	4639.07	4639.54
4	2.2760	5871.27	5863.88	5864.80	5865.12
5	2.3765	7056.74	7046.55	7048.11	7049.66
6	2.4748	8200.60	8186.74	8189.16	8191.56
7	2.5722	9303.32	9287.60	9291.11	9294.60
8	2.6694	10365.19	10348.68	10353.53	10358.34
9	2.7672	11386.35	11372.26	11378.70	11385.10
10	2.8662	12366.78	12359.17	12367.48	12375.72
11	2.9669	13306.30	13309.54	13319.98	13330.33
12	3.0702	14204.55	14227.00	14239.83	14252.57
Average percentage deviation			0.264	0.262	0.266

Hulburt-Hirschfelder function (Steele *et al* 1962) and the error involved in the curve fitting.

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