

Theoretical thermochemistry of some LiXH_n and BeXH_n compounds

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Summary. In this theoretical work, we consider the geometrical, electronic and energetic properties of some lithium and beryllium derivatives. The standard heats of formation of these compounds have been calculated at the $\text{MP4} = \text{SDTQ}/6\text{-}31 + \text{G}(2df, p) // \text{MP2} = \text{FULL}/6\text{-}31\text{G}(d, p)$ level. The values obtained at this level of the theory are also compared with the heats of formation deduced from a composite procedure in which it is assumed that some corrections can be treated separately and combined in an additive manner. We find that the values determined with the complete $6\text{-}31 + \text{G}(2df, p)$ basis set are the more accurate.

Key words: LiXH_n and BeXH_n compounds – Structures – Heats of formation

1. Introduction

Theoretical thermochemistry is now able to predict fairly accurate heats of formation for a wide range of small chemical compounds. Using large basis sets and including much of the correlation effect, the enthalpies of formation can be estimated to ± 2 kcal/mol accuracy [1–3]. Strategies have been developed by Pople and his group [1, 4, 5]. Many papers on boron chemistry [6] published in the last decade reexamined the binding energy in diborane and the related standard heats of formation (ΔH_f) of monoborane and diborane [7]. Such data are essential for evaluating thermochemical properties of larger boron derivatives and for fundamental comparisons between carbon and boron chemistry. The systematic study of small lithium and beryllium compounds was pioneered in 1977 by Dill et al. [8], based on $\text{HF}/6\text{-}31\text{G}^* // \text{HF}/\text{STO}\text{-}3\text{G}$ calculations. More recently, further work on lithium and beryllium derivatives has been published [9–14]. These papers describe the geometries and the electronic properties of these species, but only a few deal with accurate evaluation of the energy content. In this study, we attempt to obtain heats of formation for LiXH_n and BeXH_n compounds where X stands for one of the second-row atoms (Li, Be, B, C, N, O or F). We do not consider the known bridged structures [11–13]. All these results will be used later as the basic data for evaluating ΔH_f of larger Li or Be containing compounds and for establishing bond energies and stabilization energies in lithium and beryllium derivatives.

2. Theoretical methods

The theoretical methods used in this work are similar to those described previously [1, 15, 16]. We employ the spin-restricted Hartree–Fock (RHF) theory for closed-shell molecules and the unrestricted form of this theory (UHF) for open-shell systems. The equilibrium structures and the harmonic frequencies were first obtained with the 6-31G(*d, p*) basis set (or in the usual notation: HF/6-31G**//HF/6-31G**). SCF frequencies are overestimates [17–19], and so the theoretical frequencies have been rescaled (in particular, to compute the thermal corrections between 0 K, 0 vibration and 298.15 K). Beyond the Hartree–Fock level, we use Møller–Plesset perturbation theory for the correlation corrections. Fully optimized structures were obtained at full second order (MP2/6-31G**//MP2/6-31G**). More accurate energies were then obtained as single-point calculations at full fourth order (MP4*sdtq*, i.e. including single, double, triple and quadruple replacements). We employ the 6-31 + G(2*df, p*) basis set for the MP4 calculations. We also compare such MP4/6-31 + G(2*df, p*)//MP2/6-31G** energies with those available from Pople's procedure [20]. This assumes additivity of incremental effects beyond the 6-31G(*d, p*) level:

$$E[6-31 + G(2df, p)] \approx E(\text{combined}) = E[6-31 + G(d, p)] + E[6-31G(2d, p)] \\ + E[6-31G(df, p)] - 2E[6-31G(d, p)]. \quad (1)$$

3. Results and discussion

3.1. The geometries

Optimized structures are given in Table 1, together with experimental data [21] and the theoretical STO-3G geometries of Dill et al. [8]. Other theoretical results are also available [14]. The HF/6-31G** and the MP2/6-31G** geometrical parameters are nearly the same. The average difference between these two sets of results is less than 0.001 Å for the distances and 0.15° for the angles, while the corresponding standard deviations are 0.02 Å and 0.94°. Discrepancies between HF/STO-3G [8] and MP2/6-31G** values are much larger, however, with standard deviations (average differences) of 0.06 Å (0.04 Å) for the distances and 1.48° (0.60°) for the angles. Hence the effect of basis set on the geometrical parameters is important, but the correlation effect is insignificant. Moreover, polarization functions (at least *d* functions on the heavy atoms) are needed to obtain correct curvature of the potential energy surface at the stationary point. For example, at the SCF level, HBeOH has a $C_{\infty v}$ symmetry with STO-3G or 3-21G basis sets [8, 22] and is bent with 6-31G* [22] or 6-31G** basis sets (see Table 1). Nevertheless, HF/6-31G** energies for both linear and bent structures of HBeOH remain close to each other: the $C_{\infty v}$ structure is a second order transition point (Ts2), only 0.51 kcal/mol higher in energy than the C_s equilibrium geometry. Beyond the Hartree–Fock level, the energy difference increases to reach 13.77 kcal/mol at the MP4*sdtq*/combined-basis-set level. Such behavior is already known for the boron derivatives [23].

We now consider the distances between the heavy atoms. It is interesting to compare covalent radii (r_{cov} [24, 25]) with half the homonuclear single bond lengths as obtained at the MP2/6-31G** level ($d/2$) in H_nX-XH_n compounds.

Table 1. Molecular optimized structures (in Å and degrees) at the Hartree-Fock (RHF and UHF) and second order Møller-Plesset (MP2) level, using 6-31G** basis set

	Sym.	HF	MP2	[8]	[21]	Sym.	HF	MP2	[8]	[21]
$\text{LiH}(^1\Sigma^+)$	$C_{\infty v}$	Li-H	1.630	1.623	1.510	1.595	C-Be	1.544	1.607	C_{2v}
$\text{LiLi}(^1\Sigma^+)$	$D_{\infty h}$	Li-Li	2.807	2.773	2.696	2.673	C-H	1.081	1.091	
$\text{LiBeH}(^1\Sigma^+)$	$C_{\infty v}$	Be-Li	2.469	2.429	2.384		HCB	121.8	112.7	
		Be-H	1.360	1.350	1.300		HCB/HCH	158.0	127.6	
$\text{LiBH}_2(^1A_1)$	C_{2v}	B-Li	2.233	2.223	2.194		C-Be	1.669	1.661	1.652
		B-H	1.206	1.201	1.164		C-H	1.083	1.085	1.086
		HBH	110.6	110.8	112.4		HCH	111.2	111.2	111.1
$\text{CH}_3\text{Li}(^1A_1)$	C_{3v}	C-Li	2.000	2.003	2.009		C-Be	1.705	1.693	
		C-H	1.093	1.092	1.083		C-H	1.090	1.090	
		HCH	106.3	106.9			HCB	111.7	111.5	
		LiCH	112.4	111.9	112.6		C-Be	1.697	1.685	1.691
$\text{NH}_3\text{Li}(^1A_1)$	C_{2v}	N-Li	1.749	1.750	1.635		C-H	1.090	1.090	1.085
		N-H	1.003	1.013	1.026		Be-H	1.336	1.328	1.291
		NNH	105.3	104.8	102.3		HCB	112.0	111.8	111.8
		N-Li	2.063	2.062	1.944		N-Be	1.334	1.364	1.288
$\text{HLiNH}_3(^1A_1)$	C_{3v}	Li-H	1.659	1.651	1.514		N-H	0.985	0.999	1.021
		N-H	1.003	1.014	1.028		N-Be	1.482	1.485	1.438
		HNLi	111.6	112.2	113.0		N-H	0.991	1.002	1.027
		HNH	107.3	106.6			N-Be	1.501	1.504	1.457
$\text{LiOH}(^1\Sigma^+)$	$C_{\infty v}$	O-Li	1.590	1.593	1.432	1.582	N-H	0.997	1.006	1.020
		O-H	0.934	0.953	0.971	[0.97]	Be-H	1.335	1.326	1.287
$\text{LiF}(^1\Sigma^+)$	$C_{\infty v}$	F-Li	1.555	1.567	1.407	1.5631	HNBe	125.2	125.2	125.8

Table 1 (continued)

	Sym.	HF	MP2 [8]	[21]	Sym.	HF	MP2 [8]	[21]		
BeLi ₂ (¹ Σ ⁺)	D _{∞h}	Be-Li	2.563	2.517	H ₂ BeNH ₃ (¹ A')	C _s	N-Be	1.809	1.794	1.747
BHLi ₂ (¹ A ₁)	C _{2v}	B-Li	2.095	2.093			N-H	1.003	1.014	1.030
		B-H	1.195	1.195			Be-H	1.371	1.359	1.296
		LiBLi	78.7	79.1			NBeH	109.2	109.2	
CH ₂ Li ₂ (¹ A ₁)	C _{2v}	C-Li	1.971	1.973				111.7	111.7	
perpendicular form		C-H	1.099	1.098			HNB	113.1	113.7	
		HCH	107.2	107.3				109.4	109.7	
		LiCLi	119.1	117.0	BeO(¹ Σ ⁺)	C _{∞v}	O-Be	1.296	1.356	1.269
NHLLi ₂ (¹ A ₁)	C _{2v}	N-Li	1.754	1.782	BeO(³ Π)	C _{∞v}	O-Be	1.458	1.472	1.331
		N-H	1.013	1.025	HBeOH(¹ A')	C _s	O-Be	1.400	1.409	[1.463]
		LiNH	134.5	131.2			O-H	0.935	0.951	
OLi ₂ (¹ Σ _g ⁺)	D _{∞h}	O-Li	1.614	1.653			Be-H	1.332	1.324	
				[1.59]			OBeH	181.4	182.5	
HBe(² Σ ⁺)	C _{∞v}	Be-H	1.347	1.340			BeOH	138.2	138.6	
HBeH(¹ Σ _g ⁺)	D _{∞h}	Be-H	1.333	1.326	1.3431		HBeOH	180.0	180.0	
HBeBeH(¹ Σ _g ⁺)	D _{∞h}	Be-Be	2.124	2.094	[1.34]			1.707	1.692	1.582
		Be-H	1.341	1.335			O-Be	1.365	1.353	1.296
BeBH(³ Σ ⁻)	C _{∞v}	B-Be	1.642	1.649	1.744		Be-H	0.944	0.961	0.975
		Be-H	1.179	1.178	1.162		O-H	108.2	108.0	111.0
HBeBH ₂ (¹ A ₁)	C _{2v}	B-Be	1.903	1.882			OBeH	123.7	124.2	125.4
		Be-H	1.339	1.330			BeOH	1.365	1.378	1.299
		B-H	1.196	1.192			F-Be	1.329	1.323	1.285
		HBH	113.8	113.5			Be-H			

The latter are available from Table 1 for $X = \text{Li}$ and Be and from previously reported results, for $X = \text{B}$ [16]:

Li	$d/2 = 1.39 \text{ \AA}$	$r_{cov} = 1.34 \text{ \AA}$ [24]	$r_{cov} = 1.34 \text{ \AA}$ [25]
Be	$d/2 = 1.05 \text{ \AA}$	$r_{cov} = 1.25 \text{ \AA}$	$r_{cov} = 0.91 \text{ \AA}$
B	$d/2 = 0.83 \text{ \AA}$	$r_{cov} = 0.90 \text{ \AA}$	$r_{cov} = 0.82 \text{ \AA}$
C	$d/2 = 0.76 \text{ \AA}$	$r_{cov} = 0.77 \text{ \AA}$	$r_{cov} = 0.77 \text{ \AA}$
N	$d/2 = 0.72 \text{ \AA}$	$r_{cov} = 0.75 \text{ \AA}$	$r_{cov} = 0.74 \text{ \AA}$
O	$d/2 = 0.73 \text{ \AA}$	$r_{cov} = 0.73 \text{ \AA}$	$r_{cov} = 0.70 \text{ \AA}$
F	$d/2 = 0.71 \text{ \AA}$	$r_{cov} = 0.72 \text{ \AA}$	$r_{cov} = 0.68 \text{ \AA}$

$d/2$ and r_{cov} correlate with regression coefficients larger than 0.95 ($d/2 = 0.04 + 0.99r_{cov}$ for Huheey's data and $d/2 = -0.04 + 1.08r_{cov}$ for Sanderson's data). This comparison also suggests that the covalent radii for Be and B could be close to 1 Å and 0.8 Å respectively as reported by Sanderson [25].

We now turn to the other bond lengths of Table 1. Normal two-electron single bonds are expected to have lengths close to the sum of the covalent radii. The previously reported values show that Li–Be bond length in LiBeH (2.429 Å) compares nicely with the sum $D = d(\text{Be})/2 + d(\text{Li})/2 = 2.44 \text{ \AA}$. This matches the Boy's picture [26], with one centroid of charge in the Be–Li region. The same conclusion can be obtained for Li– BH_2 ($D = 2.22 \text{ \AA}$), HLi-NH_3 ($D = 2.14 \text{ \AA}$), HBe-BH_2 ($D = 1.88 \text{ \AA}$) and $\text{H}_2\text{Be-NH}_3$ ($D = 1.80 \text{ \AA}$). However, the “single” bonds Li–C in Li-CH_3 (2.00 Å from Table 1 versus $D = 2.15 \text{ \AA}$) and Be–C in HBe-CH_3 (1.69 Å from Table 1 versus $D = 1.81 \text{ \AA}$) show relatively shorter lengths than expected for covalent two-electron bonds. This shortening is usually explained by the ionic character of these bonds (see [27–29] for the C–Li bond).

3.2. Statistical thermodynamics

The classical formalism of statistical thermodynamics allows us to obtain thermal corrections

$$H^\circ(T) - H^\circ(0, 0) = ZPE + \int_{0\text{K}}^T C_p dT,$$

standard entropies and heat capacities; ZPE is the zero point energy. The vibrational frequencies have been calculated at the $\text{HF}/6\text{-}31\text{G}^{**}/\text{HF}/6\text{-}31\text{G}^{**}$ level. These quantities are known to be overestimated by approximately ten percent [17–19]. Then, one uses the following scaling procedure to correct the theoretical frequencies [18]:

$$\nu(\text{exp}) \approx \nu(\text{scaled}) = -45.99 + 0.92227\nu(\text{th}). \quad (2)$$

The results are listed in Table 2, together with some experimental values from [21]. One generally observes a satisfactory agreement between theoretical and experimental quantities.

3.3. The electronic energies

Table 3 gives total energies both at the $\text{MP4}/\text{combined-basis-set}$ (relation 1) and $\text{MP4}/6\text{-}31 + \text{G}(2df, p)$ levels. For many compounds (especially the molecules involving the lightest atoms), the additivity assumption beyond the $6\text{-}31\text{G}(d, p)$

Table 2. Thermal corrections ($H(T) - H(0\text{ K}, 0\text{ vibration})$), standard entropies and heat capacities at the harmonic level, assuming scaled theoretical frequencies

Compounds		$H^\circ(298.15) - H^\circ(0, 0)$ kcal/mol	$S^\circ(298.15)$ cal/K mol	$C_p(298.15)$ cal/K mol
LiH	th	3.89	40.89	7.12
	exp	4.09	40.85	7.11
LiLi	th	2.75	47.67	8.69
	exp	2.81	47.08	8.63
LiBeH	th	6.97	51.31	11.53
LiBH ₂	th	13.22	54.72	12.09
CH ₃ Li	th	22.70	54.37	12.42
NH ₂ Li	th	16.90	55.47	11.90
HLiNH ₃	th	28.65	62.59	16.75
LiOH	th	10.34	51.64	11.06
	[exp]	9.78	50.35	11.03
LiF	th	3.40	47.82	7.45
	exp	3.42	47.87	7.48
BeLi ₂	th	4.72	59.39	14.07
BHLi ₂	th	9.51	64.42	15.91
CH ₂ Li ₂	th	16.69	66.20	17.30
NHLi ₂	th	11.35	61.61	14.65
OLi ₂	th	5.85	57.14	12.00
	[exp]	5.88	54.76	11.89
HBe	th	4.83	42.20	6.97
	Exp	5.01	42.26	6.98
HBeH	th	9.81	42.00	8.80
	[exp]	11.37	41.37	7.26
HBeBeH	th	11.74	51.45	13.66
BeBH(³ Σ ⁻)	th	9.78	50.25	8.41
HBeBH ₂	th	18.46	56.12	13.81
BeCH ₂ (¹ A ₁)	th	15.82	55.33	11.44
BeCH ₂ (³ B ₁)	th	15.85	55.33	10.96
BeCH ₃	th	23.48	53.40	11.40
HBeCH ₃	th	28.17	55.59	13.80
BeNH(¹ Σ ⁺)	th	11.41	48.36	9.18
BeNH(³ Π)	th	9.63	50.67	8.52
HBeNH ₂	th	22.30	55.43	13.56
H ₂ BeNH ₃ ^a	th	34.79	64.51	15.60
BeO(¹ Σ ⁺)	th	4.31	47.08	7.02
	Exp	4.20	47.23	7.05
BeO(³ Π)	th	3.58	49.80	7.29
HBeOH	th	14.96	54.86	12.36
H ₂ BeOH ₂ ^a	th	26.76	64.54	15.73
HBeF	th	8.30	49.99	9.78

Experimental values are taken from the JANAF thermochemical tables [21]

Brackets mean uncertain reported experimental values

^aFree rotation assumed around the central bond

Table 3. Total energies (au), isogyric reactions and heats of formation (kcal/mol)

Method Basis set Geometry	MP4sdqtq Combined MP2/6-31G**	MP4sdqtq 6-31 + G**2df MP2/6-31G**	Isogyric reaction	ΔH_f Combined energy	ΔH_f Exact energy 6-31 + G**2df	ΔH_f Experimental (or theoretical)	Ref.
LiH	-8.01205	-8.01242	$\text{LiH} + \text{H} \rightarrow \text{Li} + \text{H}_2$	35.36	35.19	33.61 ± 0.01 33.1 (th.) 51.60 ± 0.7	[21] [1] [21]
LiLi	-14.89649	-14.89706	$\text{LiLi} + 2\text{H} \rightarrow 2\text{Li} + \text{H}_2$	50.83	50.59		
LiBeH	-22.68835	-22.68889	$\text{LiBeH} + \text{H} \rightarrow \text{Li} + \text{Be} + \text{H}_2$	73.63	73.55		
LiBH ₂	-33.35202	-33.35083	$\text{LiBH}_2 + 2\text{H} \rightarrow \text{Li} + \text{B} + 2\text{H}_2$	65.64	66.49		
LiCH ₃	-47.24631	-47.24314	$\text{LiCH}_3 + 3\text{H} \rightarrow \text{C} + \text{Li} + 3\text{H}_2$	22.52	23.10	28 (th)	[9]
NH ₂ Li	-63.31741	-63.31069	$\text{NH}_2\text{Li} + 4\text{H} \rightarrow \text{N} + \text{Li} + 3\text{H}_2$	4.71	9.93	26.7 (th)	[29]
LiHNH ₃	-64.49586	-64.49163	$\text{LiHNH}_3 + 4\text{H} \rightarrow \text{Li} + \text{N} + 4\text{H}_2$	-0.59	3.09	13.8 (th)	[9]
LiOH	-83.20272	-83.19472	$\text{LiOH} + 3\text{H} \rightarrow \text{Li} + \text{O} + 2\text{H}_2$	-62.09	-56.60	-56 ± 1.5	[21]
LiF	-107.21994	-107.21378	$\text{LiF} + 2\text{H} \rightarrow \text{Li} + \text{F} + \text{H}_2$	-89.04	-81.75	-81.45 ± 2	[21]
BeLi ₂	-29.53078	-29.53295	$\text{BeLi}_2 + 2\text{H} \rightarrow \text{Be} + 2\text{Li} + \text{H}_2$	114.35	113.30		
BHLi ₂	-40.16550	-40.14522	$\text{BHLi}_2 + 3\text{H} \rightarrow \text{B} + 2\text{Li} + 2\text{H}_2$	123.07	135.95		
CH ₂ Li ₂	-	-54.07433	$\text{CH}_2\text{Li}_2 + 4\text{H} \rightarrow \text{C} + 2\text{Li} + 3\text{H}_2$	-	67.16		
NHLi ₂	-70.16545	-70.16222	$\text{NHLi}_2 + 5\text{H} \rightarrow \text{N} + 2\text{Li} + 3\text{H}_2$	38.62	41.69	51 (th)	[9]
OLi ₂	-90.08302	-90.07246	$\text{OLi}_2 + 4\text{H} \rightarrow \text{O} + 2\text{Li} + 2\text{H}_2$	-47.35	-40.22	-39.9 ± 0.36	[21]
BeH	-15.18872	-15.18939	$\text{BeH} \rightarrow \text{Be} + \text{H}$	81.74	81.52	76.7 ± 6.7 81.7 (th.)	[21] [1]

^a Calculated from data of [28]

Table 3 (continued)

Method Basis set Geometry	MP4sdqtq Combined MP2/6-31G**	MP4sdqtq 6-31 + G**2df MP2/6-31G**	Isogyric reaction	ΔH_f Combined energy	ΔH_f Exact energy 6-31 + G**2df	ΔH_f Experimental (or theoretical)	Ref.
BeH ₂	-15.83900	-15.83948	BeH ₂ → Be + H ₂	37.82	37.74	[30] 39.5 (th.)	[21] [1]
HBeBeH	-30.49775	-30.49592	HBeBeH → 2Be + H ₂	85.51	87.07		
BeBH (³ Σ ⁻)	-39.85852	-39.85779	BeBH ⁽³⁾ → Be + B + H	169.01	169.68		
HBeBH ₂	-41.17726	-41.17543	HBeBH ₂ + H → Be + B + 2H ₂	68.20	69.60		
BeCH ₂ (¹ A ₁)	-53.75596	-53.75369	BeCH ₂ ⁽¹⁾ + 2H → Be + C + 2H ₂	116.38	116.52		
BeCH ₂ (³ B ₁)	-53.77434	-53.77247	BeCH ₂ ⁽³⁾ → Be + C + H ₂	108.97	108.85		
BeCH ₃	-54.43321	-54.43161	BeCH ₃ + H → Be + C + 2H ₂	62.32	62.05		
HBeCH ₃	-55.08429	-55.08073	HBeCH ₃ + 2H → Be + C + 3H ₂	14.49	15.47		
BeNH (¹ Σ ⁺)	-69.83558	-69.83309	BeNH ⁽¹⁾ + 3H → Be + N + 2H ₂	94.62	97.31		
BeNH (³ Π)	-69.82055	-69.81860	BeNH ⁽³⁾ + H → Be + N + H ₂	106.36	108.69		
HBeNH ₂	-71.15940	-71.15323	HBeNH ₂ + 3H → Be + N + 3H ₂	-1.61	3.42		
H ₂ BeNH ₃	-72.32465	-72.32116	H ₂ BeNH ₃ + 3H → Be + N + 4H ₂	0.95	4.32		
BeO (¹ Σ ⁺)	-89.72371	-89.71759	BeO ⁽¹⁾ + 2H → Be + O + H ₂	25.51	29.93		
BeO (³ Π)	-89.67883	-89.67862	BeO ⁽³⁾ → Be + O	57.04	57.74		
HBeOH	-91.03309	-91.02869	HBeOH + 2H → Be + O + 2H ₂	-61.26	-57.89		
H ₂ BeOH ₂	-92.16572	-92.16343	H ₂ BeOH ₂ + 2H → Be + O + 3H ₂	-39.56	-37.48		
HBeF	-115.04146	-115.03988	HBeF + H → Be + F + H ₂	-82.61	-78.05		
						32.6 ± 3.1	[21]

level gives accurate results. The standard deviation of the difference between the two sets of energies is only of 2.9 kcal/mol. Nevertheless, the combined energies are usually lower than the exact energies (the average difference is -1.7 kcal/mol) and discrepancies in the range of 4–13 kcal/mol are observed (HBeNH_2 , BeO , NH_2Li , LiF : 4 kcal/mol; LiOH : 5 kcal/mol; OLi_2 : 7 kcal/mol; BHLi_2 : 13 kcal/mol). It appears that most of the problems concern lithium containing molecules; trouble with this element has already been pointed out elsewhere [31].

3.4. The enthalpies of formation

Using the so-called “isogyric reactions” [1] reported in Table 3, one can deduce thermochemical quantities according to the following procedure:

$$\begin{aligned} \text{XYH}_n + m\text{H} &\rightarrow \text{X} + \text{Y} + \frac{1}{2}(m+n)\text{H}_2 \\ \Delta H_f(\text{XYH}_n) &= \Delta H_f(\text{X}) + \Delta H_f(\text{Y}) - m \Delta H_f(\text{H}) - \Delta H_r \\ \text{if } \Delta H_r &= \{E_X + E_Y + \frac{1}{2}(n+m)E_{\text{H}_2} - E_{\text{XYH}_n} - mE_{\text{H}}\} \\ &+ \{TC_X + TC_Y + \frac{1}{2}(n+m)TC_{\text{H}_2} - TC_{\text{XYH}_n} - mTC_{\text{H}}\}, \quad (3) \end{aligned}$$

where TC stand for the thermal corrections reported in Table 2 as $[H^\circ(298.15 \text{ K}) - H^\circ(0, 0)]$ and E are the MP4 energies from Table 3. Some additional reference data are listed in [32].

The enthalpies of formation so obtained are given in Table 3. The isogyric procedure does not cancel the errors of the combined energies. It is seen that the ΔH_f calculated using the combined energies may be quite different from those obtained using the exact energies (the difference can reach 13 kcal/mol). On the other hand, the heats of formation calculated with the MP4/6-31 + G(2df, p) energies reproduce most of the experimental data quite well. The correlation between the two sets of values is shown in Fig. 1.

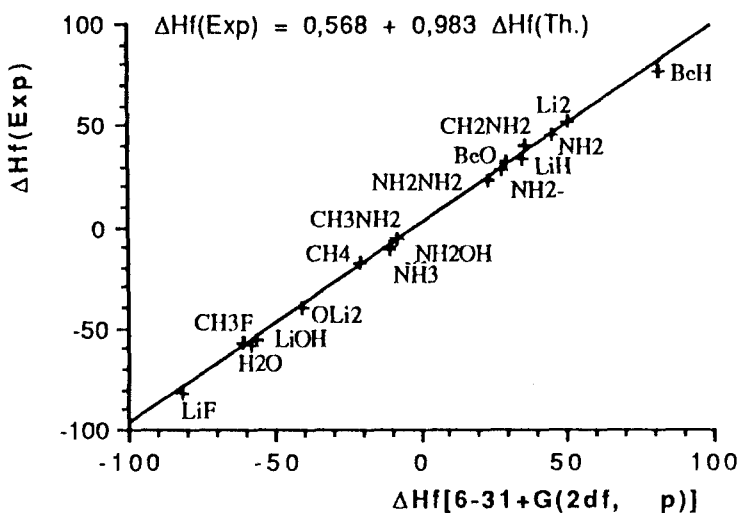


Fig. 1. Correlation between experimental and theoretical heats of formation (kcal/mol)

Recently Pople et al. have recommended that G1-theory [33] be employed for achieving a general accuracy of ± 2 kcal/mol. As shown below, this approach is similar to the strategy used in this work:

	In G1-theory	This work
Geometry:	MP2 = FULL/6-31G*	MP2 = FULL/6-31G**
Energies:	MP4/6-311G(2df, p) + correction for diffuse function + correction beyond the MP4 level	MP4 = SDTQ/6-31 + G(2df, p) diffuse function already included not included
Temperature:	ZPE only with scaled HF/6-31G* frequencies	Complete correction $H^\circ(T) - H^\circ(0, 0)$ with scaled HF/6-31G** frequencies
other:	ΔE (higher level correction)	cancel in isogyric approach

The two procedures should give results of the same quality.

Let us now consider independently some of the heats of formation given in Table 3. For BeH_2 , the value reported in the JANAF Tables (30 kcal/mol) is only a rough value; so, in accordance with Pople, we prefer the theoretical prediction [1]. The values calculated for BeH , $\text{BeO}(^1\Sigma^+)$, LiOH , LiF and OLi_2 always fall within the experimental uncertainty domain. In view of the large experimental error for BeH (± 6.7 kcal/mol), we feel that the theoretical value is more reliable. For LiH and Li_2 , theoretical values are slightly underestimated with respect to the experimental values. Extensive theoretical literature exists for methyl lithium. The theoretical C–Li bond strength calculated by Ahlrichs et al. [29] gives an enthalpy of formation of 26.7 kcal/mol. Schleyer et al. [28] report 26.9 kcal/mol. The experimental measurement of the heat of sublimation and of dissociation (methyl lithium is tetrameric in the gas phase) has not been reported, and so comparison with experimental values is not feasible for monomeric methyl lithium. Nevertheless, all the theoretical results suggest that $\Delta H_{\text{subl} + \text{diss}}(\text{CH}_3\text{Li})$ should be larger than 40 kcal/mol [34]. The studies in [28, 35] show the tetramerization energy of methyl lithium to be very large. Hence, we omit the following compounds in the comparison between theory and experiment: LiCH_3 , BeH_2 and BeH . Under this assumption, the regression showed in Fig. 1 becomes

$$\Delta H_f(\text{Exp}) = 0.893 + 0.996 \Delta H_f(6-31 + \text{G}^{**}2df) \quad (\text{with } R^2 = 0.998)$$

the average error is 0.53 kcal/mol and the standard deviation 1.25 kcal/mol.

The corresponding regression for the heats of formation deduced from the combined energy gives:

$$\Delta H_f(\text{Exp}) = 3.937 + 0.977 \Delta H_f(\text{combined}) \quad (\text{with } R^2 = 0.997)$$

the average error is 4.17 kcal/mol and the standard deviation 3.04 kcal/mol.

The theoretical results are underestimated compared with the corresponding experimental values and the approach based on the exact energies seems to be slightly more accurate than that based on the combined energies.

Finally, we briefly comment on some beryllium derivatives. Pople et al. [8] have mentioned a $^3\Pi$ electronic state for BeBH below the $^3\Sigma^-$ state. We also

obtain a $^3\Pi$ state [36], but it is found 15.2 kcal/mol higher in energy than the previous $^3\Sigma^-$ (Table 3). BeCH_2 has also a triplet state (3B_1) lower in energy than the 1A_1 state; the energy difference is of the order of 12 kcal/mol (or 7.5 kcal/mol, based on $\Delta H_f(0\text{ K})$). For the beryllium imide (BeNH), the $^1\Sigma^+$ state characterized by four π electrons is found to be 9.1 kcal/mol (11.4 kcal/mol on the $\Delta H_f(0\text{ K})$) below the $^3\Pi$. Our conclusion differs from that of Pople et al. [8]. But, as already pointed out by these authors for beryllium oxide, small basis sets incorrectly predict the ground state to be $^3\Pi$, presumably due to the lack of correlation corrections. The $^1\Sigma^+$ state of BeO is known experimentally to be the lowest singlet state. On the basis of theoretical considerations Schaefer et al. [37] reached the same conclusion. Our singlet species is 24.5 kcal/mol below the $^3\Pi$ state (27.8 kcal/mol on the $\Delta H_f(0\text{ K})$). The JANAF Tables [21] report a difference of 22.9 kcal/mol between these two states.

Conclusions

In this work we have calculated the heats of formation of some compounds containing lithium and beryllium atoms. We show that very large basis sets and electron correlation both are important to obtain accurate geometries and thermochemical properties.

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32. Compounds	MP4/Combined au	MP4/6-31 + G(2df, p) au	ΔH_f° kcal/mol [21]
H	-0.49823	-0.49823	52.103
H ₂	-1.16453	-1.16457	0.000
Li	-7.43151	-7.43158	38.074
Be	-14.61134	-14.61165	77.438
B	-24.58907	-24.58909	134.490 ^a
C	-37.76861	-37.76618	171.288
N	-54.49227	-54.49368	112.973
O	-74.93930	-74.93989	59.553
F	-99.56158	-99.56692	18.975

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