

# Gaseous Metal Hydrides $MBeH_3$ and $M_2BeH_4$ ( $M = Li, Na$ ): Quantum Chemical Study of Structure, Vibrational Spectra and Thermodynamic Properties

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**Abstract:** The theoretical study of complex hydrides  $MBeH_3$  and  $M_2BeH_4$  ( $M = Li, Na$ ) have been carried out using DFT MP2 methods with basis set 6-311++G ( $d, p$ ). The optimized geometrical parameters, vibrational spectra and thermodynamic properties of the hydrides and subunits  $MH$ ,  $M_2H^+$ ,  $M_2H_2$ ,  $BeH_2$ ,  $BeH_3^-$  have been determined. Two geometrical configurations, cyclic ( $C_{2v}$ ) and linear ( $C_{\infty v}$ ), were found for pentaatomic  $MBeH_3$  molecules, the cyclic isomer being predominant. Three isomers of  $M_2BeH_4$  molecules were revealed of the following shapes: two-cycled ( $D_{2d}$ ), polyhedral ( $C_{2v}$ ) and hexagonal ( $C_{2v}$ ). Among these structures polyhedral isomer was found to have the lowest energy. The relative abundance of the  $M_2BeH_4$  isomers in saturated vapour was analyzed. The enthalpies of formation  $\Delta_f H^\circ(0)$  of complex hydrides in gaseous phase were determined (in  $\text{kJ}\cdot\text{mol}^{-1}$ ):  $105 \pm 26$  ( $LiBeH_3$ ),  $63 \pm 37$  ( $Li_2BeH_4$ ),  $121 \pm 27$  ( $NaBeH_3$ ), and  $117 \pm 39$  ( $Na_2BeH_4$ ). The thermodynamic stability of the hydrides was examined through Gibbs free energies for heterophase decomposition.

**Keywords:** Complex Hydrides, Geometrical Structure, Vibrational Spectra, Enthalpy of Dissociation, Enthalpy of Formation, Heterophase Decomposition, Hydrogen Storage Materials

## 1. Introduction

Fossil fuels as the main source of energy worldwide are depleting, unsteady in terms of price, and have a negative impact to both the environment and humans beings [1]. Hydrogen shows a promising interest as a synthetic fuel. In order to use hydrogen as the source of energy and replacement of fossil fuels; it has to overcome three technical challenges associated with the production, storage and use [2]. Chater reported that the problem of hydrogen storage remains as the most challenging [3].

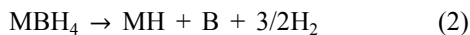
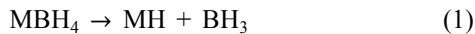
The large-scale deployment of vehicular fuel cells is hindered by the absence of a commercially feasible hydrogen storage technology. A selection of comparatively lightweight, low-cost, and high-capacity hydrogen storage devices must be available in a variety of sizes to meet different energy needs [4]. The use of hydrogen as fuel in transport offers the greatest challenge towards system design. The criteria for a

practical hydrogen store for mobile applications have been outlined by the U. S. Department of Energy [5].

Complex metal hydrides studied recently considered as promising materials for hydrogen storage [6]. When Bogdanović and Schwickardi [7] announced the reversibility of the catalyzed sodium alanate  $NaAlH_4$  in hydrogen desorption and absorption reactions at ambient condition, several researches [8-12] have been focused on alkali complex hydrides particularly in the kinetics viewpoint. The complex hydrides  $Li_2MH_5$  ( $M = B$  or  $Al$ ) were previously studied theoretically and it was shown that these materials are stable at low temperatures and suggested to be potential for hydrogen storage purposes [13]. The prediction and synthesis of hydride compound with sufficient amount of hydrogen contents were done in [14]. A lithium-hydride bonding in complexes  $HMgHLiX$  with different ligands  $X$  including hydrogen was studied theoretically at MP2/6-311++G ( $d, p$ ) level [15]. Vajeeston [16] investigated the atomic arrangements, electronic structures, and bonding nature

within the MMgH<sub>3</sub> (M = Li, Na, K, Rb, Cs) series so as to determine the stability of these materials for hydrogen storage applications.

The decomposition of the complex metal hydrides such as the alkali metal tetrahydroborides to release hydrogen gas was reported in [17] to proceed in the following two channels:



Theoretical investigation of structural, electronic and thermodynamic properties of crystalline Na<sub>2</sub>BeH<sub>4</sub> and the structural transition from  $\alpha$ - to  $\beta$ -Na<sub>2</sub>BeH<sub>4</sub> has been performed in [18].

This study aims at theoretical investigation of complex hydrides MBeH<sub>3</sub> and M<sub>2</sub>BeH<sub>4</sub> (M = Li, Na) in gaseous state implying a potential application for hydrogen storage. The content of hydrogen is 15.8% (LiBeH<sub>3</sub>), 8.6% (NaBeH<sub>3</sub>), 14.8% (Li<sub>2</sub>BeH<sub>4</sub>), and 6.8% (Na<sub>2</sub>BeH<sub>4</sub>). The targets are to determine the structure, geometrical parameters, vibrational spectra and thermodynamic properties of the complex hydrides and subunits they composed of and examine the thermodynamic stability of the hydrides with respect to different channels of decomposition. Therefore, our work will provide useful information on the structural and thermodynamic properties of the species and contribute to an exploration of the hydrides for hydrogen storage application.

## 2. Computational Details

The calculations were carried by implementing density functional theory (DFT) with hybrid functional B3PW91 [19], and second-order Møller–Plesset perturbation theory (MP2) with the basis set 6-311++G(*d*, *p*). In order to find out the accuracy of calculated results, the properties of the diatomic alkali metal hydride molecules were computed by using two different DFT hybrid functionals, B3P86 and B3PW91, and MP2 method together with the said basis set; the calculated properties were then compared with available experimental data. The optimization of geometrical parameters and vibrational spectra computations were performed using the PC GAMESS (General Atomic and Molecular Electronic Structure System) program [20], Firefly version 8.1.0 [21]. Geometrical structures and IR spectra were visualized using the wxMcMolPlt [22] and ChemCraft software [23]. The thermodynamic functions were determined in rigid rotator-harmonic oscillator approximation by using Open thermo software [24].

The enthalpies of dissociation reactions  $\Delta_r H^\circ(0)$  were computed using the formulae:

$$\Delta_r H^\circ(0) = \Delta_r E + \Delta_r \varepsilon \quad (3)$$

$$\Delta_r \varepsilon = 1/2hc(\sum \omega_{i \text{ prod}} - \sum \omega_{i \text{ react}}) \quad (4)$$

where  $\Delta_r E$  is the energy of the reaction calculated through the total energies  $E$  of the species,  $\Delta_r \varepsilon$  is the zero point vibration energy (ZPVE) correction,  $\sum \omega_{i \text{ prod}}$  and  $\sum \omega_{i \text{ react}}$  are the sums of the vibration frequencies of the products and reactants

respectively. The enthalpy of formation was computed by the underwritten equation:

$$\Delta_r H^\circ(0) = \sum \Delta_f H^\circ(0)_{\text{prod}} - \sum \Delta_f H^\circ(0)_{\text{react}} \quad (5)$$

where  $\sum \Delta_f H^\circ(0)_{\text{prod}}$  and  $\sum \Delta_f H^\circ(0)_{\text{react}}$  are enthalpies of formation of products and reactants, respectively. The values of  $\sum \Delta_f H^\circ(0)_{\text{react}}$  were taken from Ivtanthermo Database [25]. The thermodynamic stability of the complex hydrides was examined through Gibbs free energy  $\Delta_r G^\circ(T)$  of dissociation reactions. The values of  $\Delta_r G^\circ(T)$  were calculated by the formula:

$$\Delta_r G^\circ(T) = \Delta_r H^\circ(T) - T\Delta_r S^\circ(T) \quad (6)$$

where  $\Delta_r H^\circ(T)$  and  $\Delta_r S^\circ(T)$  are the enthalpy and entropy of the reaction at temperature  $T$ .

## 3. Results and Discussion

### 3.1. Subunits of Complex Hydrides

*Diatomic molecules, NaH, LiH and H<sub>2</sub>.* Two DFT hybrid functionals, B3P86 and B3PW91, together with MP2 were used to calculate molecular parameters: equilibrium internuclear distance, normal vibrational frequency, and dipole moment (Table 1). To test an accuracy of the calculated results a comparison with the available experimental data has been done. The calculated parameters do not contradict to the experimental values [26–29]. Among two DFT methods, B3PW91 and B3P86, the former provided a bit more accurate results. Thereby the results for other species considered are represented as found by DFT/B3PW91 and MP2 methods.

Table 1. Properties of diatomic molecules.

Property	DFT/B3PW91	DFT/B3P86	MP2	Expt
LiH				
$R_e(\text{Li-H})$	1.600	1.602	1.594	1.595 [27]
$-E$	8.07468	8.07418	8.02215	
$\omega_e$	1397	1400	1437	1405 [26]
$\mu_e$	5.8	5.8	6.0	5.9 [28]
NaH				
$R_e(\text{Na-H})$	1.897	1.895	1.897	1.887 [27]
$-E$	162.81202	162.82073	162.53340	
$\omega_e$	1175	1183	1192	1172 [26]
$\mu_e$	5.6	5.6	7.1	
H <sub>2</sub>				
$R_e(\text{H-H})$	0.745	0.748	0.738	0.741 [29]
$-E$	1.17858	1.17973	1.16030	
$\omega_e$	4415	4392	4534	4401 [29]

Notes: here and hereafter in Tables 2–7,  $R_e$  is the equilibrium internuclear distance in Å,  $E$  is the total energy in au,  $\omega_e$  is the vibrational frequency in cm<sup>−1</sup>,  $\mu_e$  is the dipole moment in D.

*Triatomic molecule BeH<sub>2</sub> and ions M<sub>2</sub>H<sup>+</sup> (M = Li, Na).*

The characteristics of the BeH<sub>2</sub> molecule are summarized in Table 2. The values obtained through the two methods are generally in agreement with each other and reference data [25]. The values of equilibrium internuclear distance by DFT and MP2 are slightly shorter, by 0.007 Å and 0.014 Å, than the experimental value, while the valence asymmetric frequency  $\omega_2$  is overrated by 3.2% (DFT) and 5.5% (MP2) respectively

compared to experimental magnitude. The structure of the triatomic ions  $M_2H^+$  is linear of  $D_{\infty h}$  symmetry (Fig. 1 a); the results are displayed in Table 3. The experimental reference data are not available.

**Table 2.** Properties of triatomic molecule  $BeH_2$  ( $D_{\infty h}$ ).

Property	DFT/B3PW91	MP2	Expt [30]
$R_e$ (Be-H)	1.333	1.326	1.326
$-E$	15.90487	15.83934	
$\omega_1 (\Sigma_g^+)$	2012 (0)	2064 (0)	
$\omega_2 (\Sigma_u^+)$	2228 (5.8)	2279 (5.94)	2159
$\omega_3 (\Pi_u)$	717 (15.9)	696 (16.8)	698

Note: the parenthesized values near frequencies are the IR intensities in  $D^2 \text{ amu}^{-1} \text{ \AA}^{-2}$ .

**Table 3.** Properties of triatomic ion,  $M_2H^+$  ( $M = \text{Li, Na}$ ),  $D_{\infty h}$  symmetry.

Property	DFT/B3PW91	MP2
$Li_2H^+$		
$R_e$ (M-H)	1.649	1.649
$-E$	15.44642	15.31464
$\omega_1 (\Sigma_u^+)$	428 (0)	443 (0)
$\omega_2 (\Sigma_g^+)$	1670 (11.7)	1720 (12.3)
$\omega_3 (\Pi_u)$	391 (22.2)	404 (23.9)
$Na_2H^+$		
$R_e$ (M-H)	1.972	1.974
$-E$	324.93814	324.12418
$\omega_1 (\Sigma_u^+)$	201 (0)	211 (0)
$\omega_2 (\Sigma_g^+)$	1345 (12.6)	1409 (13.3)
$\omega_3 (\Pi_u)$	357 (21.3)	378 (24.3)

The properties calculated follow the trend of that for the

diatomic molecules MH (Table 1). It is worth mentioning that the internuclear distance  $R_e(\text{Li-H})$  in  $Li_2H^+$  is longer by  $\sim 0.05 \text{ \AA}$  compared to that in LiH and  $R_e(\text{Na-H})$  in  $Na_2H^+$  is longer by  $\sim 0.08 \text{ \AA}$  than that in NaH. The vibration frequencies calculated by two methods are in a good agreement between each other, respectively.

*Tetraatomic ion  $BeH_3^-$  and molecules  $M_2H_2$  ( $M = \text{Li, Na}$ ).*

The properties of the tetraatomic species are displayed in Tables 4 and 5; their structures are shown in Figs. 1 b, c. The tetraatomic ion  $BeH_3^-$  has the planar equilibrium configuration of the  $D_{3h}$  symmetry. The values obtained through two methods are generally in agreement with each other. For the  $M_2H_2$  molecules, the values of internuclear distances, valence angles, and vibrational frequencies calculated by DFT and MP2 fairly match with each other respectively and with the theoretical results obtained previously [31]. The calculated enthalpy of dimerization for  $Li_2H_2$  is in agreement within uncertainty limit with the experimental magnitude by Wu *et al.* [32].

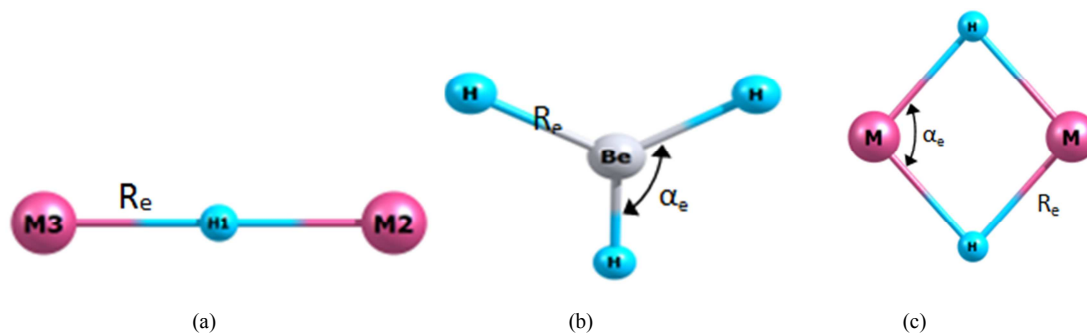
**Table 4.** Properties of tetraatomic  $BeH_3^-$  ion,  $D_{3h}$  symmetry.

Property	DFT/B3PW91	MP2
$R_e$ (Be-H)	1.423	1.415
$-E$	16.53280	16.44528
$\omega_1 (A_1')$	1673 (0)	1726 (0)
$\omega_2 (A_2')$	831 (12.8)	870 (13.9)
$\omega_3 (E')$	1673 (42.5)	1726 (43.4)
$\omega_4 (E')$	851 (8.6)	883 (10.1)

**Table 5.** Properties of dimers  $M_2H_2$  ( $M = \text{Na, Li}$ ),  $D_{2h}$  symmetry.

Property	$Li_2H_2$			$Na_2H_2$		
	DFT/B3PW91	MP2	Ref. [31]	DFT/B3PW91	MP2	Ref. [31]
$R_e$ (M-H)	1.756	1.749	1.758	2.115	2.112	2.119
$\alpha_e$ (H-M-H)	99.5	99.6	100	96.8	96.5	96
$-E$	16.22595	16.12348		325.68079	325.12896	
$\omega_1 (A_g)$	1159 (0)	1199 (0)	1194	955 (0)	1004 (0)	993
$\omega_2 (A_g)$	515 (0)	526 (0)	524	225 (0)	230 (0)	228
$\omega_3 (B_{1g})$	886 (0)	911 (0)	902	636 (0)	697 (0)	690
$\omega_4 (B_{1u})$	592 (17.6)	607 (18.6)	604	444 (19.3)	459 (21.5)	458
$\omega_5 (B_{2u})$	967 (22.2)	990 (23.9)	985	783 (22.8)	832 (25.4)	823
$\omega_6 (B_{3u})$	1066 (21.7)	1100 (22.3)	1091	819 (24.1)	869 (25.0)	855
$-\Delta E_{\text{dim}}$	201.1	207.9	204 [30]	149.0	163.2	
$-\Delta_f H^\circ(0)_{\text{dim}}$	186.8	193.2	220 $\pm$ 42 [31]	140.0	153.0	

Note: Here and hereafter  $\alpha_e$  is bond angle in degrees; the values  $\Delta E_{\text{dim}}$  and  $\Delta_f H^\circ(0)_{\text{dim}}$  are the energies and enthalpies of dimerization reactions  $2MH = M_2H_2$  in  $\text{kJ mol}^{-1}$ .



**Figure 1.** Equilibrium geometrical structure of the species: (a)  $M_2H^+$   $D_{\infty h}$ ; (b) dimers  $M_2H_2$ ,  $D_{2h}$ ; (c)  $BeH_3^-$ ,  $D_{3h}$ .

### 3.2. Geometrical Structure and Vibrational Spectra of Pentaatomic Molecules $LiBeH_3$ and $NaBeH_3$

Two possible geometrical configurations, cyclic ( $C_{2v}$ ) and linear ( $C_{\infty v}$ ), were considered for pentaatomic  $MBeH_3$  molecules (Fig. 2). The calculated equilibrium geometrical parameters and vibrational frequencies for cyclic isomer are shown in Table 6. The binding in the cyclic isomer may be considered through an attachment of  $M^+$  cation to  $BeH_3^-$  anion. Within the  $MBeH_3$  molecules, the fragment  $BeH_3$  is distorted compared to free  $BeH_3^-$  anion. In the latter the bond lengths and angles are equivalent,  $R_e(Be-H) \approx 1.42$  Å (Table 4) while in the  $MBeH_3$  molecules the bridge distances  $R_e(Be-H)$  are elongated to 1.44-1.45 Å; and the terminal distance is

shortened to  $\sim 1.35$  Å; the bond angles become also non-equivalent, the angle  $\beta_e(H_4-Be_1-H_5)$  decreases to  $104^\circ$  in  $LiBeH_3$  and  $110^\circ$  in  $NaBeH_3$ . Thus the  $BeH_3$  moiety looks alike in both  $LiBeH_3$  and  $NaBeH_3$  molecules.

The IR spectra of  $MBeH_3$  ( $C_{2v}$ ) molecules are presented in Fig. 3. The similarity of the vibrational bands is observed for  $LiBeH_3$  and  $NaBeH_3$ . For instance the most intensive bands correspond to the Be-H stretching vibrations at  $1528$   $cm^{-1}$  ( $LiBeH_3$ ) and  $1555$   $cm^{-1}$  ( $NaBeH_3$ ). The highest vibration frequencies correspond to the  $Be_1-H_3$  stretching vibrations at  $2029$   $cm^{-1}$  ( $LiBeH_3$ ) and  $1980$   $cm^{-1}$  ( $NaBeH_3$ ). The bending vibration H-Be-H is observed at  $849$   $cm^{-1}$  ( $LiBeH_3$ ) and  $833$   $cm^{-1}$  ( $NaBeH_3$ ).

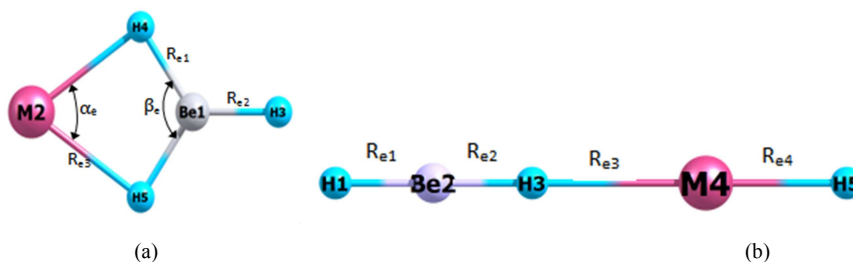


Figure 2. Equilibrium geometrical structure of  $MBeH_3$  ( $M = Li, Na$ ) molecules: (a) cyclic,  $C_{2v}$ ; (b) linear,  $C_{\infty v}$ .

Table 6. Properties of  $MBeH_3$  ( $M = Li, Na$ ) molecules ( $C_{2v}$ ).

Property	$LiBeH_3$		$NaBeH_3$	
	DFT/B3PW91	MP2	DFT/B3PW91	MP2
$R_{e1}(Be_1-H_4)$	1.452	1.446	1.444	1.437
$R_{e2}(Be_1-H_3)$	1.352	1.345	1.361	1.355
$R_{e3}(M_2-H_5)$	1.740	1.733	2.099	2.097
$\alpha_e(H_4-M_2-H_5)$	82.5	82.2	69.0	68.3
$\beta_e(H_4-Be_1-H_5)$	104.3	103.9	110.7	109.9
$-E$	24.05487	23.93721	178.78495	178.44385
$\omega_1(A_1)$	2029 (7.08)	2078 (7.52)	1980 (7.41)	2026 (8.38)
$\omega_2(A_1)$	1622 (6.10)	1667 (6.59)	1618 (7.16)	1665 (7.99)
$\omega_3(A_1)$	1207 (9.94)	1252 (10.9)	1114 (4.88)	1160 (6.39)
$\omega_4(A_1)$	594 (1.32)	606 (1.41)	389 (1.18)	394 (1.24)
$\omega_5(B_1)$	1528 (13.8)	1561 (14.6)	1555 (15.3)	1595 (16.5)
$\omega_6(B_1)$	1106 (3.09)	1142 (3.65)	982 (3.64)	1017 (4.23)
$\omega_7(B_1)$	579 (0.72)	604 (0.76)	492 (0.38)	513 (0.39)
$\omega_8(B_2)$	849 (10.2)	882 (11.0)	833 (10.6)	868 (11.6)
$\omega_9(B_2)$	327 (0.09)	337 (0.05)	266 (0.04)	265 (0.02)

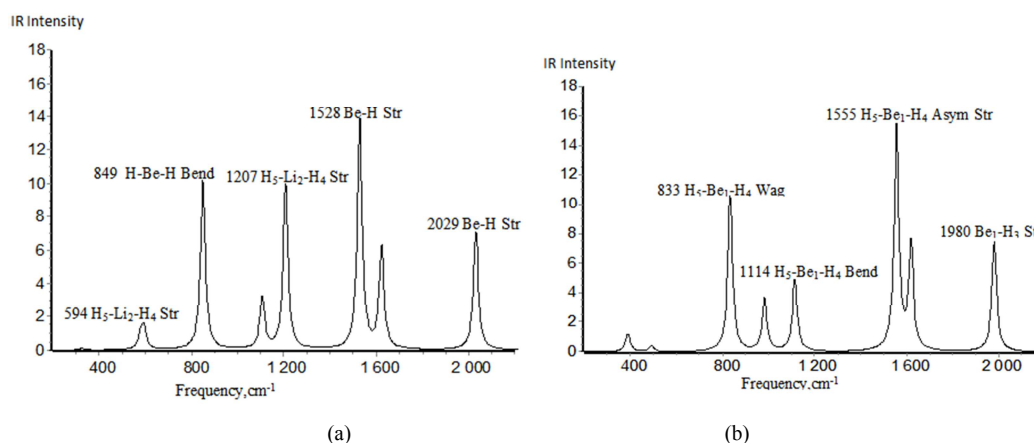


Figure 3. IR spectra of  $MBeH_3$  ( $M = Li, Na$ ) molecules,  $C_{2v}$  isomer, calculated by DFT/B3PW91: (a)  $LiBeH_3$  (b)  $NaBeH_3$ .

Table 7. Properties of  $MBeH_3$  ( $M = Li, Na$ ) molecules ( $C_{\infty}$ ).

Property	LiBeH <sub>3</sub>		NaBeH <sub>3</sub>	
	DFT/B3PW91	MP2	DFT/B3PW91	MP2
$R_{e1}(Be_2-H_1)$	1.323	1.316	1.326	1.318
$R_{e2}(Be_2-H_3)$	1.337	1.328	1.339	1.330
$R_{e3}(M_4-H_3)$	1.914	1.869	2.351	2.299
$R_{e4}(M_4-H_5)$	1.613	1.608	1.909	1.914
$-E$	23.99016	23.87426	178.72323	178.38096
$\Delta_r E_{iso}$	169.9	165.3	162.0	165.1
$\omega_1 (\Sigma^+)$	2283(9.64)	2343(10.08)	2255(8.43)	2317(9.07)
$\omega_2 (\Sigma^+)$	2082(1.68)	2145(1.36)	2038(1.62)	2106(1.63)
$\omega_3 (\Sigma^+)$	1366(7.36)	1396(7.88)	1151(8.07)	1169(9.20)
$\omega_4 (\Sigma^+)$	252(0.01)	276(0.03)	142(0.04)	166(0.03)
$\omega_5 (\Pi)$	698(17.3)	701(17.9)	748(16.4)	763(17.4)
$\omega_6 (\Pi)$	214(6.74)	210(2.38)	198(0.93)	226(0.06)
$\omega_7 (\Pi)$	30(17.4)	57(22.3)	77(20.4)	67(23.8)

Note:  $\Delta_r E_{iso}$  is the relative energy of linear isomer regarding cyclic,  $\Delta_r E_{iso} = E_{lin} - E_{cycl}$ , in  $\text{kJ mol}^{-1}$ .

The properties of the  $MBeH_3$  molecules of linear configuration are shown in Table 7. The linear isomer  $MBeH_3$  may be represented through linkage of the MH and  $BeH_2$  molecules. Worth to mention that for lithium bonding complexes  $HMgH \cdots LiH$  the linear structure was considered in [15], while existence of possible isomers had not been taken into account. Our results for  $MBeH_3$  show that the energy of the linear isomer appeared to be much higher compared to the cyclic one, *i. e.* by  $165 \text{ kJ mol}^{-1}$  (MP2, both for  $LiBeH_3$  and  $NaBeH_3$ ). It is also worth to note a low frequency of vibration  $\omega_7$  which corresponds to bending of the Li-H-Be fragment. Moreover when the parameters of the linear isomers were calculated using DFT/P3P86 method the imaginary frequency for  $LiBeH_3$  was revealed which indicates low stability of the linear structure with respect to bending deformation. Hence only this cyclic isomer was considered further in examination of thermodynamic properties of  $MBeH_3$  hydrides.

### 3.3. Geometrical Structure and Vibrational Spectra of Heptaatomic $Li_2BeH_4$ and $Na_2BeH_4$ Molecules

Several different geometrical shapes of the  $M_2BeH_4$  molecules have been considered: bipyramidal one with a tail of  $C_{2v}$  symmetry; polyhedral (compact or hat-shaped),  $C_{2v}$ ; two-cycles,  $D_{2d}$ ; and hexagonal shape,  $C_{2v}$ . Among these four configurations the first one was found to be unstable as

imaginary vibrational frequencies were revealed. The rest three structures were proved to correspond to the minima at the potential energy surface and therefore appeared to be isomers of  $M_2BeH_4$  molecules. Hereafter these isomers are denoted as I, II, and III, for  $C_{2v}$  compact,  $D_{2d}$ , and  $C_{2v}$  hexagonal, respectively; the equilibrium geometrical configurations are shown in Fig. 4 and the parameters are displayed in Tables 8-10.

The binding in the polyhedral and two-cycled structures may be considered through an attachment of two M atoms to a slightly distorted tetrahedral  $BeH_4$  moiety. In the first isomer there are two types of Be-H bonds with internuclear separations  $R_{e1}(Be-H) \approx 1.53 \text{ \AA}$  and  $R_{e2}(Be-H) \approx 1.42 \text{ \AA}$ ; the averaged of these two values,  $1.47 \text{ \AA}$ , is very close to the distance  $R_e(Be-H)$  in the  $D_{2d}$  isomer. The averaged valence angle H-Be-H in  $BeH_4$  fragment of the polyhedral isomers is about  $109^\circ$  that is almost equal to the tetrahedral angle. In the  $D_{2d}$  isomer, the angle H-Be-H is  $104^\circ$  ( $Li_2BeH_4$ ) and  $110^\circ$  ( $Na_2BeH_4$ ) that is also close to the tetrahedral angle. The hexagonal molecule may be considered through a combination of  $BeH_3^-$  and  $M_2H^+$  subunits. The geometrical parameters, the bridge Be-H bond lengths ( $\sim 1.42 \text{ \AA}$ ) and valence angle  $\beta_e(H-Be-H) \approx 117^\circ$ , of the hexagonal  $M_2BeH_4$  molecules are similar to the respective parameters in free  $BeH_3^-$  ion as well as in cyclic  $MBeH_3$  molecules.

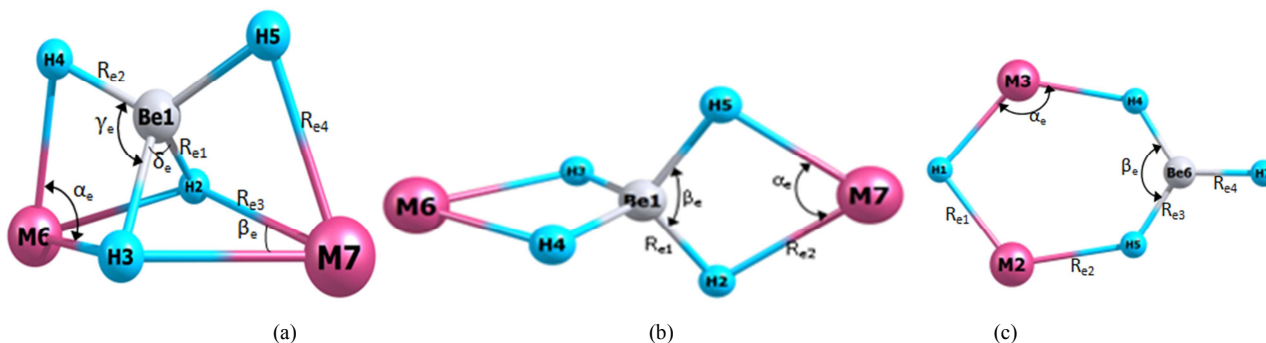


Figure 4. Equilibrium geometrical configurations of  $M_2BeH_4$  isomers: (a) I, polyhedral ( $C_{2v}$ ); (b) II, two-cycled ( $D_{2d}$ ); (c) III, hexagonal ( $C_{2v}$ ).

**Table 8.** Properties of M<sub>2</sub>BeH<sub>4</sub> (M = Li, Na) molecules (C<sub>2v</sub>, compact structure).

Property	Li <sub>2</sub> BeH <sub>4</sub>		Na <sub>2</sub> BeH <sub>4</sub>	
	DFT/B3PW91	MP2	DFT/B3PW91	MP2
R <sub>e1</sub> (Be <sub>1</sub> -H <sub>2</sub> )	1.530	1.525	1.533	1.528
R <sub>e2</sub> (Be <sub>1</sub> -H <sub>4</sub> )	1.413	1.406	1.430	1.422
R <sub>e3</sub> (M <sub>7</sub> -H <sub>2</sub> )	1.865	1.863	2.252	2.247
R <sub>e4</sub> (M <sub>7</sub> -H <sub>5</sub> )	1.822	1.82	2.126	2.125
α <sub>e</sub> (H <sub>3</sub> -M <sub>6</sub> -H <sub>4</sub> )	78.0	77.8	66.5	66.2
β <sub>e</sub> (H <sub>3</sub> -M <sub>7</sub> -H <sub>2</sub> )	70.4	70.2	60.7	60.3
γ <sub>e</sub> (H <sub>3</sub> -Be <sub>1</sub> -H <sub>4</sub> )	104.1	104.2	108.2	108.1
δ <sub>e</sub> (H <sub>3</sub> -Be <sub>1</sub> -H <sub>2</sub> )	89.3	89.2	95.8	95.2
−E	32.20966	32.03993	341.66059	341.04435
ω <sub>1</sub> (A <sub>1</sub> )	1702(1.52)	1743(1.68)	1622(3.16)	1663(3.47)
ω <sub>2</sub> (A <sub>1</sub> )	1409(8.62)	1448(8.67)	1338(11.2)	1371(11.9)
ω <sub>3</sub> (A <sub>1</sub> )	1015(4.97)	1061(8.68)	994(1.67)	1046(2.43)
ω <sub>4</sub> (A <sub>1</sub> )	1004(8.11)	1043(6.67)	936(7.75)	997(10.0)
ω <sub>5</sub> (A <sub>1</sub> )	639(1.31)	651(1.47)	387(1.66)	397(1.75)
ω <sub>6</sub> (A <sub>1</sub> )	275(0.23)	282(0.70)	132(0.41)	136(0.40)
ω <sub>7</sub> (A <sub>2</sub> )	1038(0)	1072(0)	961(0)	999(0)
ω <sub>8</sub> (A <sub>2</sub> )	476(0)	492(0)	333(0)	357(0)
ω <sub>9</sub> (B <sub>1</sub> )	1772(13.7)	1810(14.7)	1650(17.3)	1696(19.4)
ω <sub>10</sub> (B <sub>1</sub> )	1106(9.36)	1146(10.6)	1038(6.60)	1094(8.89)
ω <sub>11</sub> (B <sub>1</sub> )	741(0.45)	755(0.42)	643(0.05)	675(0.08)
ω <sub>12</sub> (B <sub>1</sub> )	674(5.41)	686(5.93)	459(4.73)	466(4.98)
ω <sub>13</sub> (B <sub>2</sub> )	1259(13.8)	1282(14.5)	1207(17.5)	1230(18.4)
ω <sub>14</sub> (B <sub>2</sub> )	894(5.76)	934(7.20)	845(7.37)	890(9.44)
ω <sub>15</sub> (B <sub>2</sub> )	384(0.02)	389(0.24)	270(0.03)	283(0.03)
μ <sub>e</sub>	5.6	5.8	7.7	8.2

**Table 9.** Properties of M<sub>2</sub>BeH<sub>4</sub> (M = Li, Na) molecules (D<sub>2d</sub>).

Property	Li <sub>2</sub> BeH <sub>4</sub>		Na <sub>2</sub> BeH <sub>4</sub>	
	DFT/B3PW91	MP2	DFT/B3PW91	MP2
R <sub>e1</sub> (Be <sub>1</sub> -H <sub>2</sub> )	1.471	1.464	1.477	1.470
R <sub>e2</sub> (M <sub>7</sub> -H <sub>2</sub> )	1.718	1.715	2.060	2.060
α <sub>e</sub> (H <sub>2</sub> -M <sub>7</sub> -H <sub>5</sub> )	84.9	84.5	72.3	71.5
β <sub>e</sub> (H <sub>2</sub> -Be <sub>1</sub> -H <sub>5</sub> )	104.1	103.9	110.8	109.9
−E	32.20384	32.03404	341.65577	341.03837
Δ <sub>r</sub> E <sub>iso</sub> (I-II)	15.3	15.5	12.6	15.7
ω <sub>1</sub> (A <sub>1</sub> )	1537(0)	1573(0)	1497(0)	1533(0)
ω <sub>2</sub> (A <sub>1</sub> )	1221(0)	1261(0)	1122(0)	1165(0)
ω <sub>3</sub> (A <sub>1</sub> )	457(0)	464(0)	222(0)	225(0)
ω <sub>4</sub> (B <sub>1</sub> )	733(0)	758(0)	769(0)	795(0)
ω <sub>5</sub> (B <sub>2</sub> )	1520(17.9)	1554(19.2)	1440(24.2)	1474(26.2)
ω <sub>6</sub> (B <sub>2</sub> )	1213(21.3)	1259(24.2)	1118(13.2)	1160(15.6)
ω <sub>7</sub> (B <sub>2</sub> )	701(4.43)	717(4.5)	506(3.65)	514(3.82)
ω <sub>8</sub> (E)	1436(30.0)	1464(32.5)	1408(35.5)	1441(39.0)
ω <sub>9</sub> (E)	1107(7.0)	1144(8.98)	957(7.86)	996(11.32)
ω <sub>10</sub> (E)	706(2.90)	729(3.58)	596(1.42)	613(1.76)
ω <sub>11</sub> (E)	101(7.58)	114(7.84)	26(7.36)	21(8.08)

Note: Δ<sub>r</sub>E<sub>iso</sub>(I-II) is the energy of isomerization reaction M<sub>2</sub>BeH<sub>4</sub> (I, C<sub>2v, comp</sub>) = M<sub>2</sub>BeH<sub>4</sub> (II, D<sub>2d</sub>), Δ<sub>r</sub>E<sub>iso</sub>(I-II) = E(II) − E(I), in kJ·mol<sup>−1</sup>.

The IR spectra of three isomers of Li<sub>2</sub>BeH<sub>4</sub> and Na<sub>2</sub>BeH<sub>4</sub> molecules are presented in Fig. 5. By comparing IR spectra of Li<sub>2</sub>BeH<sub>4</sub> and Na<sub>2</sub>BeH<sub>4</sub> molecules, alike features may be observed for the isomers of the same symmetry. For the



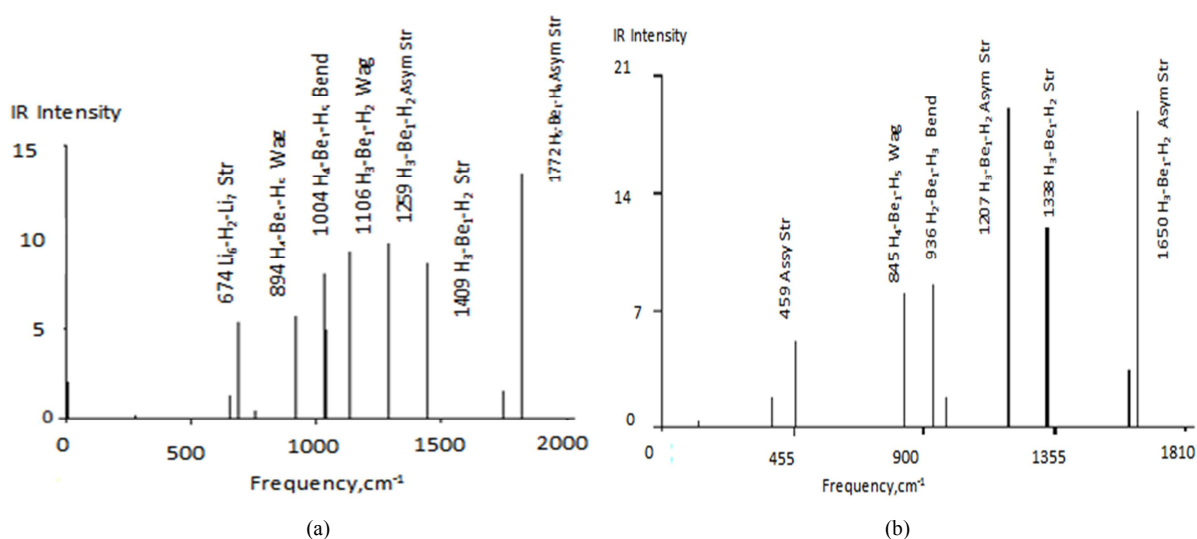
polyhedral isomer I, the bands of high intensity at  $1259\text{ cm}^{-1}$ ,  $1772\text{ cm}^{-1}$  ( $\text{Li}_2\text{BeH}_4$ ) and  $1207\text{ cm}^{-1}$ , and  $1650\text{ cm}^{-1}$  ( $\text{Na}_2\text{BeH}_4$ ) correspond to H-Be-H asymmetrical stretching vibrations of  $\text{BeH}_4$  moiety. For the two-cycled  $D_{2d}$  isomer, similar H-Be-H asymmetrical stretching vibrations of  $\text{BeH}_4$  moiety are observed at  $1436\text{ cm}^{-1}$ ,  $1520\text{ cm}^{-1}$  ( $\text{Li}_2\text{BeH}_4$ ) and  $1408\text{ cm}^{-1}$ ,  $1440\text{ cm}^{-1}$  ( $\text{Na}_2\text{BeH}_4$ ). The most intensive band in spectrum of  $\text{Li}_2\text{BeH}_4$   $D_{2d}$  is seen at  $1213\text{ cm}^{-1}$  and corresponds to the H-Li-H asymmetrical stretching mode, in  $\text{Na}_2\text{BeH}_4$   $D_{2d}$  the similar vibration is observed at  $1118\text{ cm}^{-1}$ . For the hexagonal

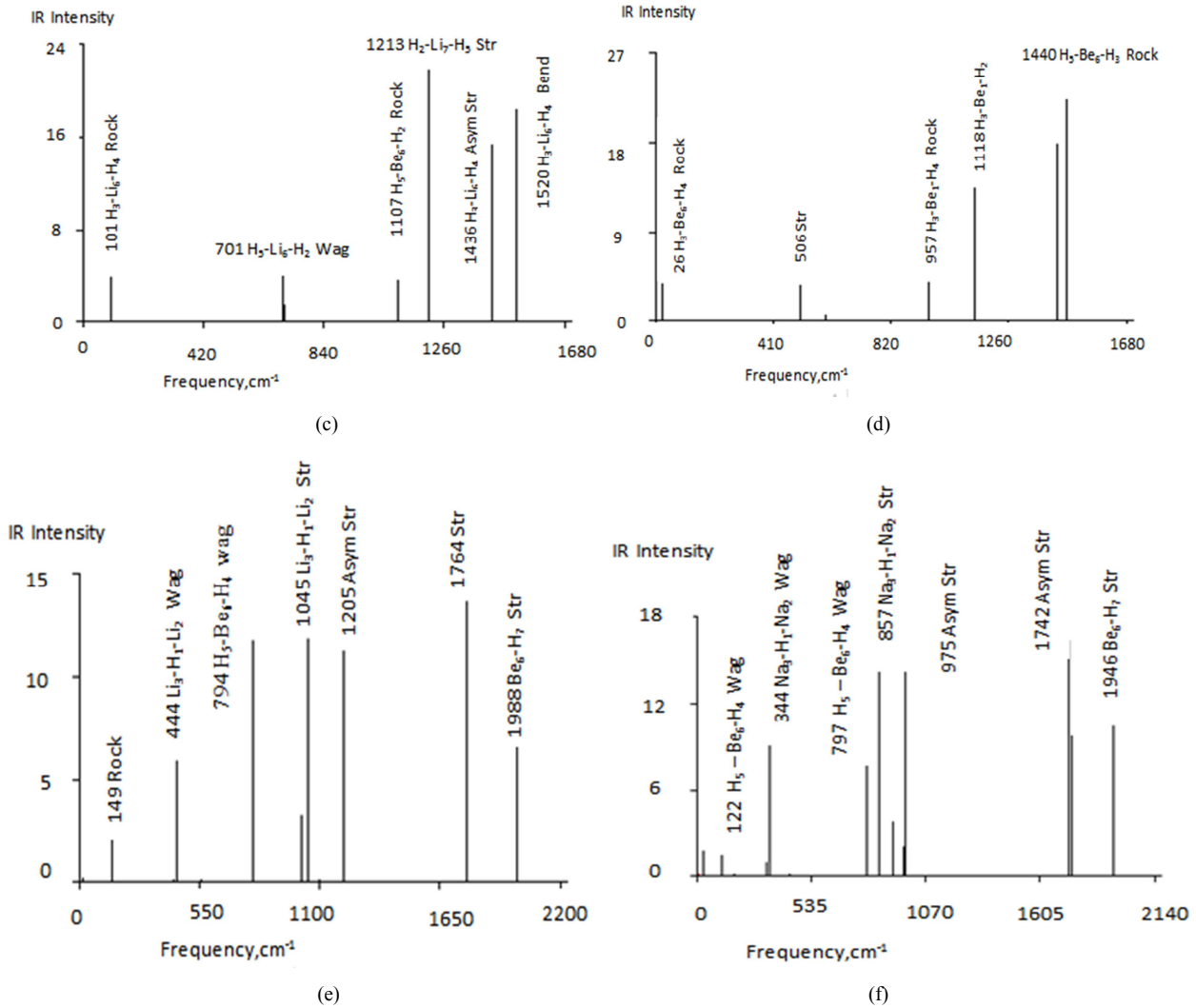
isomer the most intense bands appear at  $1764\text{ cm}^{-1}$  ( $\text{Li}_2\text{BeH}_4$ ) and  $1742\text{ cm}^{-1}$  ( $\text{Na}_2\text{BeH}_4$ ) and are characterized by stretching modes of the  $\text{BeH}_3$  fragment. Other similarities may be noted between two hexagonal species as wagging vibrations at  $444\text{ cm}^{-1}$  Li-H-Li,  $794\text{ cm}^{-1}$  H-Be-H ( $\text{Li}_2\text{BeH}_4$ ) and  $344\text{ cm}^{-1}$  Na-H-Na,  $797\text{ cm}^{-1}$  H-Be-H ( $\text{Na}_2\text{BeH}_4$ ). The vibration of highest frequency at about  $2000\text{ cm}^{-1}$ , both for  $\text{Li}_2\text{BeH}_4$  and  $\text{Na}_2\text{BeH}_4$ , corresponds to the terminal bond Be-H stretching mode, that is the highest frequency correlates with the shortest bond length  $R_e(\text{Be-H}) = 1.36\text{ \AA}$ .

Table 10. Properties of  $M_2\text{BeH}_4$  ( $M = \text{Li}, \text{Na}$ ) molecules ( $C_{2v}$ , hexagonal structure).

Property	$\text{Li}_2\text{BeH}_4$		$\text{Na}_2\text{BeH}_4$	
	DFT/B3PW91	MP2	DFT/B3PW91	MP2
$R_{e1}(\text{M}_2\text{-H}_1)$	1.705	1.700	2.050	2.049
$R_{e2}(\text{M}_2\text{-H}_5)$	1.704	1.696	2.046	2.046
$R_{e3}(\text{Be}_6\text{-H}_5)$	1.426	1.421	1.425	1.418
$R_{e4}(\text{Be}_6\text{-H}_7)$	1.357	1.352	1.365	1.360
$\alpha_e(\text{H}_1\text{-M}_3\text{-H}_4)$	127.7	126.7	119.3	118.1
$\beta_e(\text{H}_4\text{-Be}_6\text{-H}_5)$	118.2	116.7	117.1	116.4
$-E$	32.19484	32.028467	341.65258	341.03774
$\Delta E_{\text{iso}}(\text{I-III})$	38.9	30.1	21.0	17.4
$\mu_e$	4.5	4.6	5.4	5.5
$\omega_1(A_1)$	1988(7.94)	2033(8.62)	1946(9.37)	1988(10.1)
$\omega_2(A_1)$	1764(13.4)	1817(10.5)	1754(8.74)	1806(9.26)
$\omega_3(A_1)$	1090(2.29)	1130(2.20)	971(1.83)	1011(2.33)
$\omega_4(A_1)$	1045(11.6)	1067(12.5)	857(12.8)	866(13.6)
$\omega_5(A_1)$	429(0.61)	446(0.57)	325(0.88)	333(0.92)
$\omega_6(A_1)$	382(0.33)	386(0.40)	174(0.14)	176(0.16)
$\omega_7(A_2)$	234(0)	252(0)	180(0)	185(0)
$\omega_8(B_1)$	1763(9.07)	1808(14.4)	1742(14.8)	1791(16.2)
$\omega_9(B_1)$	1205(11.1)	1243(12.1)	975(12.8)	1005(13.9)
$\omega_{10}(B_1)$	1015(3.19)	1042(4.05)	917(3.44)	949(3.99)
$\omega_{11}(B_1)$	553(1.05)	569(1.07)	435(0.10)	442(0.09)
$\omega_{12}(B_1)$	150(1.61)	175(2.04)	35(1.55)	64(1.69)
$\omega_{13}(B_2)$	794(11.6)	835(12.3)	797(10.6)	839(11.7)
$\omega_{14}(B_2)$	445(5.83)	454(6.52)	344(8.17)	345(9.28)
$\omega_{15}(B_2)$	149(1.95)	153(1.54)	122(1.27)	113(1.29)
$\mu_e$	4.5	4.6	5.4	5.5

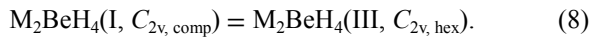
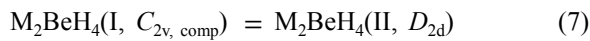
Note:  $\Delta E_{\text{iso}}(\text{I-III})$  is the energy of isomerization reaction  $M_2\text{BeH}_4 (\text{I}, C_{2v, \text{comp}}) = M_2\text{BeH}_4 (\text{III}, C_{2v, \text{hex}})$ ,  $\Delta E_{\text{iso}}(\text{I-III}) = E(\text{III}) - E(\text{I})$ , in  $\text{kJ}\cdot\text{mol}^{-1}$ .





**Figure 5.** IR spectra of complex hydrides  $M_2BeH_4$  ( $M = Li, Na$ ) calculated by DFT/B3PW91: (a)  $Li_2BeH_4$  ( $C_{2v}$ , compact); (b)  $Na_2BeH_4$  ( $C_{2v}$ , compact); (c)  $Li_2BeH_4$  ( $D_{2d}$ ); (d)  $Na_2BeH_4$  ( $D_{2d}$ ); (e)  $Li_2BeH_4$  ( $C_{2v}$ , hexagonal); (f)  $Na_2BeH_4$  ( $C_{2v}$ , hexagonal).

The relative energies  $\Delta_r E_{iso}$  of the isomers II and III regarding I given in Tables 9, 10 were calculated for the following isomerisation reactions:



The values of  $\Delta_r E_{iso}$  are positive: for reaction R1 15.5 kJ mol<sup>-1</sup> ( $Li_2BeH_4$ ), 15.7 kJ mol<sup>-1</sup> ( $Na_2BeH_4$ ), and for R2 30.1 kJ mol<sup>-1</sup> ( $Li_2BeH_4$ ), 17.4 kJ mol<sup>-1</sup> ( $Na_2BeH_4$ ) according to MP2 calculations. Therefore among three isomers, I, II, and III, the first one has the lowest energy, followed by  $D_{2d}$ , and the hexagonal:  $E(I) < E(II) < E(III)$  for both molecules. The energy difference between isomers II and III is 14.6 kJ mol<sup>-1</sup> ( $Li_2BeH_4$ ), and 1.7 kJ mol<sup>-1</sup> ( $Na_2BeH_4$ ) in favour of  $D_{2d}$ , thus worth to note the isomers II and III of the  $Na_2BeH_4$  molecule are comparable by energy.

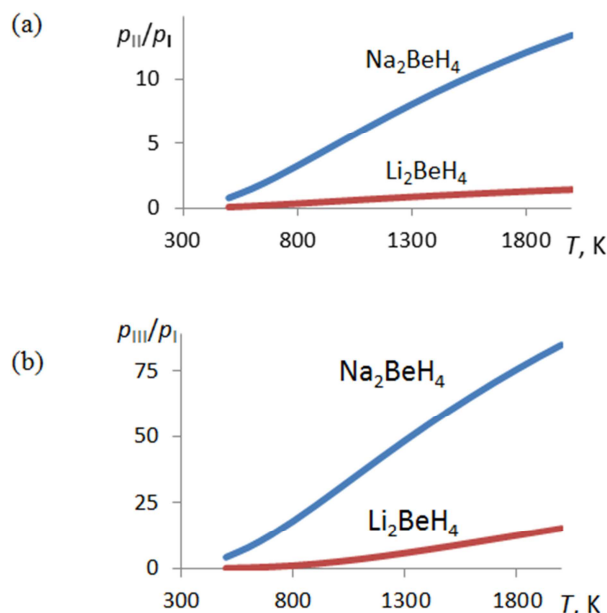
To evaluate the relative concentration of the isomers in the equilibrium vapour, the thermodynamic approach was applied. The following equation was used:

$$\Delta_r H^\circ(0) = T\Delta_r \Phi^\circ(T) - RT \ln \left( \frac{p_A}{p_B} \right) \quad (9)$$

where  $\Delta_r H^\circ(0)$  is the enthalpy of isomerisation of the reaction;  $T$  is absolute temperature;  $\Delta_r \Phi^\circ(T)$  is the reduced Gibbs energy of the reaction,  $\Phi^\circ(T) = -[H^\circ(T) - H^\circ(0) - TS^\circ(T)]/T$ ;  $p_A/p_B$  is the pressure ratio between two isomers, that is  $p_{II}/p_I$  for reaction R1 and  $p_{III}/p_I$  for R2. The values of  $\Delta_r H^\circ(0)$  were calculated using isomerization energies  $\Delta_r E_{iso}$  and the ZPVE corrections  $\Delta_r \epsilon$  by Eqs. (3) and (4). The relative concentrations  $p_A/p_B$  have been calculated for the temperature range between 500 and 2000 K; the plots are shown in Fig. 6. The graphs show that the relative concentrations of the isomers II and III increase with temperature increase for both molecules, for  $Li_2BeH_4$  the growth is slow compared to  $Na_2BeH_4$ . At 1000 K for  $Li_2BeH_4$  and  $Na_2BeH_4$  the values of  $p_{II}/p_I$  are equal to 0.6 and 5.2, respectively, while the ratios  $p_{III}/p_I$  are 2.5 and 30, respectively. Therefore the isomer I of  $Li_2BeH_4$  molecule is more abundant at moderate temperatures, but at higher temperatures its concentration is noticeably decreasing. For  $Na_2BeH_4$  the hexagonal isomer is much more abundant compared to either



isomers I and II. The fraction of each isomer of  $\text{Na}_2\text{BeH}_4$  was estimated as  $x_i = p_i/(p_I + p_{II} + p_{III})$  where i stands for I, II, or III, the results for two selected temperatures are given in Table 11. Thus as seen the hexagonal isomer of  $\text{Na}_2\text{BeH}_4$  is predominant in a broad temperature range and its concentration is increasing with temperature raise.



**Figure 6.** Relative abundance  $p_A/p_B$  versus temperature for three isomers of complex hydrides  $\text{M}_2\text{BeH}_4$  by MP2 method: (a)  $p_{II}(\text{D}_{2d})/p_I(\text{C}_{2v}, \text{comp})$ ; (b)  $p_{III}(\text{C}_{2v}, \text{hex})/p_I(\text{C}_{2v}, \text{comp})$ .

**Table 11.** The fraction  $x_i$  of isomers I, II, and III in equilibrium vapour of  $\text{Na}_2\text{BeH}_4$ .

T, K	$x_I$	$x_{II}$	$x_{III}$
500	0.26	0.22	0.52
1000	0.03	0.14	0.83

**Table 12.** The energies and enthalpies of gas-phase dissociation reactions, and enthalpies of formation of gaseous complex hydrides  $\text{LiBeH}_3$  and  $\text{Li}_2\text{BeH}_4$ ; all values are given in  $\text{kJ mol}^{-1}$ .

No	Reaction	Method	$\Delta_r E$	$\Delta_r \varepsilon$	$\Delta_f H^\circ(0)$	$\Delta_f H^\circ(0)$
1	$\text{LiBeH}_3 = \text{LiH} + \text{BeH}_2$	DFT/B3PW91	197.77	-16.57	181.20	83.76
		MP2	198.81	-17.67	181.14	83.82
2	$\text{LiBeH}_3 = \text{Li} + \text{Be} + 3/2\text{H}_2$	DFT/B3PW91	382.73	-19.28	363.49	114.00
		MP2	360.87	-19.90	340.98	136.51
3	$\text{Li}_2\text{BeH}_4 = \text{LiBeH}_3 + \text{LiH}$	DFT/B3PW91	210.31	-61.09	149.22	73.98
		MP2	211.54	-62.74	148.79	74.47
4	$\text{Li}_2\text{BeH}_4 = 2\text{LiH} + \text{BeH}_2$	DFT/B3PW91	408.08	-35.38	372.70	31.70
		MP2	410.34	-36.96	373.38	31.02
5	$\text{Li}_2\text{BeH}_4 = \text{Li}_2\text{H}_2 + \text{BeH}_2$	DFT/B3PW91	207.0	-21.09	185.91	29.60
		MP2	202.43	-22.26	180.2	35.30
6	$\text{Li}_2\text{BeH}_4 = 2\text{LiH} + \text{Be} + \text{H}_2$	DFT/B3PW91	589.47	-42.90	546.57	52.06
		MP2	580.64	-44.14	536.50	62.13
7	$\text{Li}_2\text{BeH}_4 = 2\text{Li} + \text{Be} + 2\text{H}_2$	DFT/B3PW91	596.61	-33.21	563.40	71.82
		MP2	564.18	-34.23	529.95	105.29
8	$\text{Li}_2\text{BeH}_4 = \text{Li}_2\text{H}^+ + \text{BeH}_3^-$	DFT/B3PW91	603.02	-23.96	579.67	
		MP2	605.02	-23.64	581.38	

### 3.4. Thermodynamic Properties of Complex Hydrides

#### 3.4.1. The Enthalpies of Dissociation Reactions and Enthalpies of Formation of Molecules

Different dissociation reactions of the complex hydrides  $\text{MBeH}_3$  and  $\text{M}_2\text{BeH}_4$  have been examined; for the latter the polyhedral isomer of  $\text{C}_{2v}$  symmetry was considered as lowest by energy. The calculated energies and enthalpies of gas-phase reactions are represented in Tables 9 and 10; the results obtained by DFT/B3PW91 and MP2 methods. Two types of dissociation reactions of complex hydrides,  $\text{MBeH}_3$  and  $\text{M}_2\text{BeH}_4$  were considered: a partial dissociation and complete reduction of the hydride with hydrogen gas release. The values of  $\Delta_r H^\circ(0)$  show that all reactions proceed with the absorption of energy (endothermic). The partial dissociation of both penta- and heptaatomic hydrides requires much less energy than reaction with hydrogen formation. The most energy consuming reactions are those with  $\text{H}_2$  evolving (reactions 2 for  $\text{MBeH}_3$  and 6, 7 for  $\text{M}_2\text{BeH}_4$ ) and dissociation into ionic subunits  $\text{M}_2\text{H}^+$  and  $\text{BeH}_3^-$  (reactions 8).

The enthalpies of formation  $\Delta_f H^\circ(0)$  of the complex hydrides were calculated through the enthalpies of the reactions and enthalpies of formation of the gaseous products, Li, Na,  $\text{H}_2$ , LiH, NaH [25] and  $\text{BeH}_2$  [27]. The enthalpies of formation of  $\text{M}_2\text{H}_2$  molecules involved in reactions 5 were obtained through the enthalpies of dimerization reactions (Table 5), the averaged values of  $\Delta_f H^\circ(0)$  between DFT/B3PW91 and MP2 methods were accepted:  $90 \pm 10 \text{ kJ mol}^{-1}$  ( $\text{Li}_2\text{H}_2$ ) and  $139 \pm 10 \text{ kJ mol}^{-1}$  ( $\text{Na}_2\text{H}_2$ ). The enthalpies of formation of the penta- and heptaatomic hydrides are presented in the far right column in Tables 12, 13. The enthalpies of formation of  $\text{MBeH}_3$  molecules are accepted as the averaged values found through the enthalpies of reactions 1 and 2; similarly for  $\text{M}_2\text{BeH}_4$  through reactions 3-7. Uncertainties were estimated as half-differences between maximum and minimum magnitudes. The accepted values of  $\Delta_f H^\circ(0)$  are gathered in Table 14.

**Table 13.** The energies and enthalpies of gas-phase dissociation reactions, and enthalpies of formation of gaseous complex hydrides NaBeH<sub>3</sub> and Na<sub>2</sub>BeH<sub>4</sub>; all values are given in kJ mol<sup>-1</sup>.

No	Reaction	Method	$\Delta_r E$	$\Delta_r \epsilon$	$\Delta_f H^\circ(0)$	$\Delta_f H^\circ(0)$
1	NaBeH <sub>3</sub> = NaH + BeH <sub>2</sub>	DFT/B3PW91	178.71	-14.22	164.49	103.83
		MP2	186.70	-15.59	171.31	97.01
2	NaBeH <sub>3</sub> = Na + Be + 3/2H <sub>2</sub>	DFT/B3PW91	311.65	-15.58	296.07	131.44
		MP2	320.36	-15.73	304.63	151.34
3	Na <sub>2</sub> BeH <sub>4</sub> = NaBeH <sub>3</sub> + NaH	DFT/B3PW91	167.02	-55.09	111.94	134.69
		MP2	176.20	-57.50	118.69	121.12
4	Na <sub>2</sub> BeH <sub>4</sub> = 2NaH + BeH <sub>2</sub>	DFT/B3PW91	345.74	-28.63	317.11	94.01
		MP2	362.90	-30.95	331.94	79.18
5	Na <sub>2</sub> BeH <sub>4</sub> = Na <sub>2</sub> H <sub>2</sub> + BeH <sub>2</sub>	DFT/B3PW91	196.74	-19.59	177.14	87.50
		MP2	199.66	-20.75	178.90	85.70
6	Na <sub>2</sub> BeH <sub>4</sub> = 2NaH + Be + H <sub>2</sub>	DFT/B3PW91	527.13	-36.15	490.98	114.37
		MP2	533.19	-38.14	495.05	110.30
7	Na <sub>2</sub> BeH <sub>4</sub> = 2Na + Be + 2H <sub>2</sub>	DFT/B3PW91	430.22	-23.81	406.41	128.87
		MP2	403.86	-25.30	378.57	156.71
8	Na <sub>2</sub> BeH <sub>4</sub> = Na <sub>2</sub> H <sup>+</sup> + BeH <sub>3</sub> <sup>-</sup>	DFT/B3PW91	499.40	-18.58	480.00	
		MP2	497.94	-17.95	480.00	

**Table 14.** Accepted enthalpies of formation (in kJ mol<sup>-1</sup>) of gaseous complex hydrides MBeH<sub>3</sub> and M<sub>2</sub>BeH<sub>4</sub> (M = Li, Na).

Hydride	$\Delta_f H^\circ(0)$	Hydride	$\Delta_f H^\circ(0)$
LiBeH <sub>3</sub>	105 ± 26	NaBeH <sub>3</sub>	121 ± 27
Li <sub>2</sub> BeH <sub>4</sub>	63 ± 37	Na <sub>2</sub> BeH <sub>4</sub>	117 ± 39

Stability of the gaseous complex hydrides MBeH<sub>3</sub> and M<sub>2</sub>BeH<sub>4</sub> regarding heterophase decomposition with hydrogen release were also considered. The enthalpies of the heterophase reactions were calculated and given in Table 12. The required enthalpies of formation of Be, LiH, NaH, Li, Na in condensed phase were taken from [25]. In the heterophase reactions considered, beryllium is in solid state, the alkali metal hydrides are in gas-phase (reactions 1, 4) or in condensed phase (reactions 2, 5); complete decomposition is described by reactions 3, 6. The results show that the reactions in which gaseous MH are among the products are endothermic, while the rest reactions are exothermic; the biggest energy being released in reactions 2 and 5 with MH<sub>(c)</sub>.

### 3.4.2. Thermal Stability of the Complex Hydrides and Thermodynamic Favourability of the Reactions

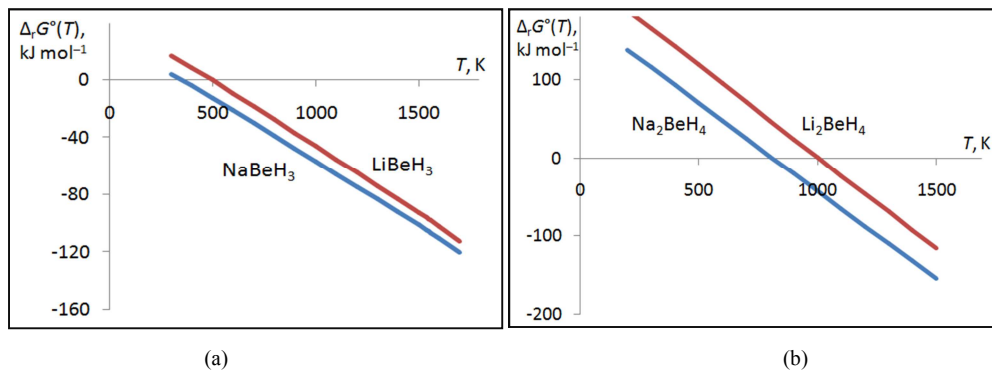
The thermodynamic stability of the complex hydrides MBeH<sub>3</sub> and M<sub>2</sub>BeH<sub>4</sub> was examined through Gibbs free energies for heterophase reactions shown in Table 15. The temperature dependences of  $\Delta_r G^\circ$  are presented in Figs. 7-9. For the reactions in which MH is in gaseous phase  $\Delta_r G^\circ$  are negative at moderate and elevated temperatures (Fig. 7); the decomposition reactions are thermodynamically favoured at

temperatures above 350 K (NaBeH<sub>3</sub>), 500 K (LiBeH<sub>3</sub>), 800 K (Na<sub>2</sub>BeH<sub>4</sub>) and 1000 K (Li<sub>2</sub>BeH<sub>4</sub>). Thus the MBeH<sub>3</sub> hydrides appeared to be less stable thermodynamically than M<sub>2</sub>BeH<sub>4</sub> and Na-containing hydrides are less stable compared to Li-hydrides.

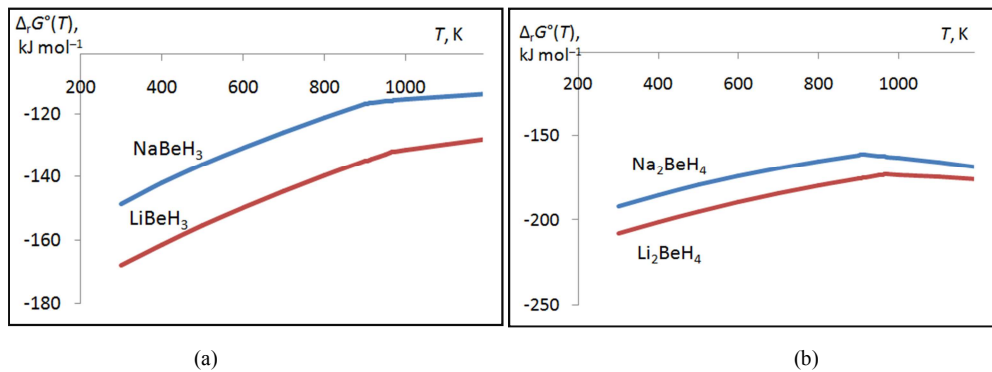
For reactions in which both MH and Be are in condensed phase (Fig. 8) the values of  $\Delta_r G^\circ(T)$  are negative for whole temperature range considered. The Na-containing hydrides are slightly more stable than Li-hydrides as the values of  $\Delta_r G^\circ(T)$  for the former are less negative. The inflections on the curves correspond to phase change transition of the products, namely the melting points of LiH<sub>(c)</sub> and NaH<sub>(c)</sub> at 965 K and 911 K [25], respectively. The Gibbs free energy for the decomposition reaction of MBeH<sub>3</sub> decreases with temperature raise, while for M<sub>2</sub>BeH<sub>4</sub> hydrides the values of  $\Delta_r G^\circ$  pass through maximum at temperatures of the phase transitions. Here the entropy has an impact on  $\Delta_r G^\circ(T)$ : as a jump of entropy at phase transition of MH<sub>(c)</sub> occurs hence the contribution of entropy factor  $T\Delta_r S$  increases with temperature raise.

**Table 15.** The enthalpies of heterophase dissociation reactions of gaseous hydrides MBeH<sub>3</sub> and M<sub>2</sub>BeH<sub>4</sub>.

No	Reaction	$\Delta_r H^\circ(0)$ , kJ mol <sup>-1</sup>	
		M = Li	M = Na
1	MBeH <sub>3</sub> = MH <sub>(g)</sub> + Be <sub>(c)</sub> + H <sub>2(g)</sub>	34	22
2	MBeH <sub>3</sub> = MH <sub>(c)</sub> + Be <sub>(c)</sub> + H <sub>2(g)</sub>	-191	-173
3	MBeH <sub>3</sub> = M <sub>(c)</sub> + Be <sub>(c)</sub> + 3/2H <sub>2(g)</sub>	-105	-121
4	M <sub>2</sub> BeH <sub>4</sub> = 2MH <sub>(g)</sub> + Be <sub>(c)</sub> + H <sub>2(g)</sub>	220	172
5	M <sub>2</sub> BeH <sub>4</sub> = 2MH <sub>(c)</sub> + Be <sub>(c)</sub> + H <sub>2(g)</sub>	-234	-221
6	M <sub>2</sub> BeH <sub>4</sub> = 2M <sub>(c)</sub> + Be <sub>(c)</sub> + 2H <sub>2(g)</sub>	-63	-117



**Figure 7.** Gibbs free energy  $\Delta_r G^\circ(T)$  against temperature for heterophase decomposition reactions of complex hydrides  $\text{MBeH}_3$  and  $\text{M}_2\text{BeH}_4$ : (a)  $\text{MBeH}_{3(\text{g})} = \text{MH}_{(\text{g})} + \text{Be}_{(\text{c})} + \text{H}_{2(\text{g})}$ ; (b)  $\text{M}_2\text{BeH}_{4(\text{g})} = 2\text{MH}_{(\text{g})} + \text{Be}_{(\text{c})} + \text{H}_{2(\text{g})}$ .

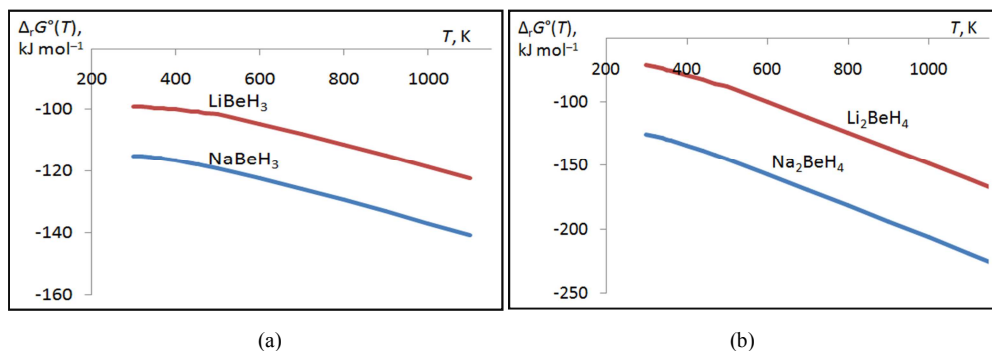


**Figure 8.** Gibbs free energy  $\Delta_r G^\circ(T)$  against temperature for heterophase decomposition reactions of complex hydrides  $\text{MBeH}_3$  and  $\text{M}_2\text{BeH}_4$ : (a)  $\text{MBeH}_{3(\text{g})} = \text{MH}_{(\text{c})} + \text{Be}_{(\text{c})} + \text{H}_{2(\text{g})}$ ; (b)  $\text{M}_2\text{BeH}_{4(\text{g})} = 2\text{MH}_{(\text{c})} + \text{Be}_{(\text{c})} + \text{H}_{2(\text{g})}$ .

For the reactions with complete dissociation into alkaline metal and beryllium in condensed phase (Fig. 9) the Gibbs free energies are negative in the temperature range considered and decreasing with temperature increase, this indicates that the decomposition processes are spontaneous. In contrast to previous case (Fig. 8), the Na-containing hydrides are less stable than Li-hydrides as the values of  $\Delta_r G^\circ(T)$  are less negative for the latter.

For different channels of dissociation of the hydrides, a correlation between  $\Delta_r G^\circ(T)$  and  $\Delta_r H^\circ(0)$  values may be noted: the lower is the enthalpy of the reaction the more negative are  $\Delta_r G^\circ(T)$  and hence the more favourable the decomposition process. For instance, for the reactions with gaseous alkali hydrides  $\text{MH}$  the enthalpies  $\Delta_r H^\circ(0)$  are positive,  $\sim 20$ – $30$   $\text{kJ}$

$\text{mol}^{-1}$  ( $\text{MBeH}_3$ ) and  $\sim 170$ – $220$   $\text{kJ mol}^{-1}$  ( $\text{M}_2\text{BeH}_4$ ); then the Gibbs free energies are positive at low and moderate temperatures and turn negative at certain temperatures said (Fig. 7). This implies that the reversibility of the reactions is able to be attained. For other heterogeneous reactions the  $\Delta_r H^\circ(0)$  values are negative, the Gibbs free energies are negative (Figs. 8, 9) that is the decomposition of the hydrides, both  $\text{MBeH}_3$  and  $\text{M}_2\text{BeH}_4$ , is spontaneous in the whole temperature range considered. The reaction with Li/Na and Be in condensed phase the reversibility may be achieved by pressure increase (Le Châtelier's principle). The reversibility of the decomposition reactions of hydrides is one of the requirements for hydrogen storage materials.



**Figure 9.** Gibbs free energy  $\Delta_r G^\circ(T)$  against temperature for heterophase decomposition reactions of complex hydrides  $\text{MBeH}_3$  and  $\text{M}_2\text{BeH}_4$ : (a)  $\text{MBeH}_{3(\text{g})} = \text{M}_{(\text{c})} + \text{Be}_{(\text{c})} + 3/2\text{H}_{2(\text{g})}$ ; (b)  $\text{M}_2\text{BeH}_{4(\text{g})} = 2\text{M}_{(\text{c})} + \text{Be}_{(\text{c})} + 2\text{H}_{2(\text{g})}$ .

## 4. Conclusion

The geometrical parameters, vibrational spectra and thermodynamic properties of the complex hydrides  $MBeH_3$  and  $M_2BeH_4$  ( $M = Li, Na$ ) and subunits have been determined using DFT/B3PW91 and MP2 methods. The results obtained by both methods are in a good agreement between each other and with the reference data available for subunits  $MH$ ,  $BeH_2$ ,  $M_2H_2$ . The enthalpies of different gas-phase dissociation reactions were computed; the enthalpies of formation of the complex hydrides were found. The Gibbs free energies  $\Delta_r G^\circ(T)$  of heterophase decomposition of  $MBeH_3$  and  $M_2BeH_4$  with hydrogen release were analyzed. It was shown the reactions the products of which were gaseous alkaline metals and solid beryllium may be reversible at moderate temperatures. The reactions of complete decomposition (products are  $M_{(c)}$ ,  $Be_{(c)}$ ,  $H_2$ ) were shown to be spontaneous at a broad temperature range; the reversibility of the reactions may be attained if certain conditions are provided. The complex hydrides  $MBeH_3$  and  $M_2BeH_4$  ( $M = Na$  or  $Li$ ) may be considered as promising candidates for hydrogen storage applications as they showed the feasibility of hydrogen gas production.

## Authors' Contributions

Authors participated equally in all steps to the completion of this work.

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## References

- [1] Patlitzianas, K. D., Doukas, H., Kagiannas, A. G., and Psarras, J., *Sustainable energy policy indicators: Review and recommendations*. Renewable Energy, 2008. 33(5): p. 966-973.
- [2] Sartbaeva, A., Kuznetsov, V., Wells, S., and Edwards, P., Energy Environ. Sci. 2008, 1, 79 Armaroli, N., Balzani, V. Chem Sus Chem, 2011. 4: p. 21.
- [3] Chater, P. A., Mixed anion complex hydrides for hydrogen storage. 2010, University of Birmingham.
- [4] Alapati, S. V., Johnson, J. K., and Sholl, D. S., Identification of destabilized metal hydrides for hydrogen storage using first principles calculations. J. Phys. Chem. B, 2006. 110(17): p. 8769-8776.
- [5] Ahluwalia, R., Hua, T., and Peng, J., On-board and off-board performance of hydrogen storage options for light-duty vehicles. Int. J. Hydrogen Energy, 2012. 37(3): p. 2891-2910.
- [6] Jena, P., Superhalogens: A Bridge between Complex Metal Hydrides and Li Ion Batteries. J. Phys. Chem. Lett., 2015. 6(7): p. 1119-1125.
- [7] Bogdanović, B., and Schwickardi, M., Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. J. Alloys Compd., 1997. 253: p. 1-9.
- [8] Zaluska, A., Zaluski, L., and Ström-Olsen, J., Nanocrystalline magnesium for hydrogen storage. J. Alloys Compd., 1999. 288(1): p. 217-225.
- [9] Zidan, R. A., Takara S., Hee, A. G., and Jensen, C. M., Hydrogen cycling behavior of zirconium and titanium-zirconium-doped sodium aluminum hydride. J. Alloys Compd., 1999. 285(1): p. 119-122.
- [10] Fletcher, G., Schmidt, M., and Gordon, M., Developments in parallel electronic structure theory. Adv. Chem. Phys., 1999. 110: p. 267-294.
- [11] Sandrock, G., Gross, K., and Thomas, G., Effect of Ti-catalyst content on the reversible hydrogen storage properties of the sodium alanates. J. Alloys Compd., 2002. 339(1): p. 299-308.
- [12] Morioka, H., Kakizaki, K., Chung, S. C., and Yamada, A., Reversible hydrogen decomposition of  $KAlH_4$ . J. Alloys Compd., 2003. 353(1): p. 310-314.
- [13] Melkizedeck Hiiti Tsere, Tatiana P. Pogrebnaya, Alexander M. Pogrebnoi. Complex Hydrides  $Li_2MH_5$  ( $M = B, Al$ ) for Hydrogen Storage Application: Theoretical Study of Structure, Vibrational Spectra and Thermodynamic Properties. *International Journal of Computational and Theoretical Chemistry*. Vol. 3, No. 6, 2015, pp. 58-67. doi: 10.11648/j.ijctc.20150306.13.
- [14] Nakamori, Y., Miwa, K., Ninomiya, A., Li, H., Ohba, N., Towata S. I., Züttel, A. and Orimo, S. I., Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativities: First-principles calculations and experiments. Phys. Rev. B, 2006. 74(4): p. 045126.
- [15] Li, Q., Wang, Y., Li, W., Cheng, J., Gong, B., and Sun, J., Prediction and characterization of the  $HMgHLiX$  ( $X = H, OH, F, CCH, CN$ , and  $NC$ ) complexes: a lithium-hydride lithium bond. Phys. Chem. Chem. Phys., 2009. 11(14): p. 2402-2407.
- [16] Vajeeston, P., Ravindran, P., Kjekshus, A., and Fjellvåg, H., First-principles investigations of the  $MMgH_3$  ( $M = Li, Na, K, Rb, Cs$ ) series. J. Alloys Compd., 2008. 450(1): p. 327-337.
- [17] Züttel, A., Wenger, P., Rentsch, S., Sudan, P., Mauron, P., and Emmenegger, C.,  $LiBH_4$  a new hydrogen storage material. J. Power Sources, 2003. 118(1): p. 1-7.
- [18] Hu, C., Wang, Y., Chen, D., Xu, D., and Yang, K., First principles calculations of structural, electronic and thermodynamic properties of  $Na_2BeH_4$ . Physical Review B, 2007. 76(14): p 144104.
- [19] Becke, A. D., Density - functional thermochemistry. III. The role of exact exchange. J. Phys. Chem., 1993. 98(7): p. 5648-5652.
- [20] Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, K. A., Nguyen, K. A. and Su, S. General atomic and molecular electronic structure system. J. Comput. Chem., 1993. 14(11): p. 1347-1363.
- [21] Granovsky, A. A., Firefly version 8.1.0, [www http://classic.chem.msu.su/gran/firefly/index.html](http://classic.chem.msu.su/gran/firefly/index.html).

- [22] Bode, B. M. and Gordon M. S., MacMolPlt: a graphical user interface for GAMESS. *J. Mol. Graphics Modell.*, 1998. 16(3): p. 133-138.
- [23] Zhurko, G. and Zhurko, D., Chemcraft, Version 1.7 (build 365). 2013.
- [24] Tokarev, K. L., "OpenThermo", v. 1.0 Beta 1 (C) ed., 2007-2009. <http://openthermo.software.informer.com/>.
- [25] Gurvich, L. V., Yungman, V. S., Bergman, G. A., Veitz, I. V., Gusarov, A. V., Iorish V. S., Leonidov, V. Y., Medvedev, V. A., Belov, G. V., Aristova, N. M., Gorokhov, L. N., Dorofeeva, O. V., Ezhov, Y. S., Efimov, M. E., Krivosheya, N. S., Nazarenko, I. I., Osina, E. L., Ryabova, V. G., Tolmach, P. I., Chandamirova, N. E., Shenyavskaya, E. A., "Thermodynamic Properties of individual Substances. Ivtanthermo for Windows Database on Thermodynamic Properties of Individual Substances and Thermodynamic Modeling Software", Version 3.0 (Glushko Thermocenter of RAS, Moscow, 1992-2000).
- [26] Irikura, K. K., "Experimental Vibrational Zero-Point Energies: Diatomic Molecules" *J. Phys. Chem. Ref. Data* 36(2), 389, 2007.
- [27] NIST Diatomic Spectral Database ([www.physics.nist.gov/PhysRefData/MolSpec/Diatomic/index.html](http://www.physics.nist.gov/PhysRefData/MolSpec/Diatomic/index.html)).
- [28] NIST Chemistry Webbook (<http://webbook.nist.gov/chemistry>).
- [29] Huber, K.P.; Herzberg, G., *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* Van Nostrand Reinhold Co., 1979.
- [30] Jacox, M. E., *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*, *J. Phys. Chem. Ref. Data*, Monograph 3 (1994) (updated data in NIST Chemistry Webbook - <http://webbook.nist.gov/chemistry/>).
- [31] Chen, Y. L., Huang C. H., and Hu, W. P., Theoretical study on the small clusters of LiH, NaH, BeH<sub>2</sub>, and MgH<sub>2</sub>. *J. Phys. Chem. A*, 2005. 109(42): p. 9627-9636.
- [32] Wu, C. and Ihle, H., *Thermochemistry of the Dimer Lithium Hydride Molecule Li<sub>2</sub>H<sub>2</sub> (g)*. 1982.