

## Study of Dehydrogenation of Pressure-induced NaBH<sub>4</sub> Structures Using Calculated NQCC Parameters

M.A. Rafiee\*

Department of Chemistry, Payame Noor University, P. O. Box: 19395-3697 Tehran, Iran

(Received 15 March 2018, Accepted 28 June 2018)

Nuclear quadrupole resonance (NQR) spectroscopy is an accurate method for determination of electric charge distribution around quadrupolar nuclei. Using *ab initio* computational methods, it is possible to calculate nuclear quadrupole coupling constants (NQCCs) with high accuracy, and obtain the useful structural information using these parameters. Sodium borohydride, NaBH<sub>4</sub>, as a metal hydride complex, is an appropriate candidate for the use in fuel cells as hydrogen storage material with high capacity of 10.6 wt%. Despite the high capacity of hydrogen storage, hydrogen desorption occurs at high temperatures due to high stability and strong bonds of this compound. This problem limits the practical usage of NaBH<sub>4</sub> in fuel cells. One way to overcome this problem is applying the high-pressure techniques and using the pressure-induced NaBH<sub>4</sub> structures. Under ambient conditions, NaBH<sub>4</sub> has a cubic structure ( $\alpha$ -NaBH<sub>4</sub>) that can be converted to  $\beta$ - and  $\gamma$ -NaBH<sub>4</sub> by increasing the pressure. In the present research, charge distribution of  $\alpha$ -NaBH<sub>4</sub> nanocrystal has been compared to that of high-pressure structures using calculated NQCCs to study the effect of pressure on different NaBH<sub>4</sub> structures and their hydrogen desorption ability. Our results show the smaller value of <sup>2</sup>H-NQCCs and higher value of <sup>11</sup>B-NQCCs for  $\beta$ -NaBH<sub>4</sub> respect to other structures. In other words, the B-H bond is weaker in  $\beta$ -NaBH<sub>4</sub>, and it is expected that dehydrogenation occurs more feasible at lower temperatures in  $\beta$ -phase compared to other phases. NBO results are in agreement with calculated NQCCs. Calculations were performed using Gaussian 09 program in B3LYP/6-311G\*.

**Keywords:** Nuclear quadrupole resonance (NQR), Sodium borohydride (NaBH<sub>4</sub>), Hydrogen storage, *Ab initio* calculations

### INTRODUCTION

The structural investigation on metal borohydrides is of particular importance due to their high gravimetric hydrogen content. Sodium borohydride (NaBH<sub>4</sub>) is a potential hydrogen storage material with hydrogen storage capacity of 10.6 wt% [1,2].

Based on the relevant studies, the alkali aluminum tetrahydrides, with a general formula (MAIH<sub>4</sub>; M = Na, Li), are considered as a class of promising candidates for on-board applications [3,4]. In comparison, borohydrides have much higher storage capacities (up to 18.2 wt%). Additionally, borohydrides are lighter compounds due to

presence of boron atom instead of the metal atom in the chemical structures. It has been reported that application of NaBH<sub>4</sub> and other M-BH<sub>4</sub> (M = Li, Mg and Ca) compounds is accompanied with difficulties due to their high stability, and, hence, high desorption temperatures. The reported desorption temperatures for NaBH<sub>4</sub> fall in the range of 400-595 °C [5-7]. The reason of these high desorption temperatures is the presence of the strong covalent and ionic bonds in these compounds. Therefore, many efforts have been made to improve the properties of the original NaBH<sub>4</sub>. In this regard, various approaches have been proposed such as chemical destabilization, catalytic doping, nanoconfinement, and combination of these methods [8-10]. Synthetic methods based on high-pressure techniques are active areas of research [11,12] for developing the new

\*Corresponding author. E-mail: rafiee.marjan@gmail.com

hydride compounds (high-pressure phases) with better desorption properties.

Understanding the B-H bond nature is essential for improving the dehydrogenation performance. For this purpose, nuclear quadrupole resonance (NQR) spectroscopy [13] can be used as a useful method for calculating the charge density distribution, and understanding the B-H bond strength.

NQR spectroscopy is a susceptible method for calculating the electric charge distribution of quadrupolar nuclei ( $I > 1/2$ ). The charge distribution of molecules and complexes can be defined using the quantum mechanical approach [13] while the resultant electric field gradient (EFG) of total molecular charges can be evaluated at any point in the molecular space. The quadrupolar nuclei possess a nuclear electric quadrupole moment ( $Q$ ). The nuclear electric quadrupole moment of the atomic nucleus interacts with EFG at the nucleus site resulting in interaction energy which is called nuclear quadrupole coupling constant (NQCC) [14-16]. Therefore, the components of the NQCC tensor can be obtained by quantum chemical calculation of the expectation values of the EFG tensor components. The NQCC of a nucleus is a perfect criterion for determination of the charge density at the nucleus. In the present manuscript, calculated NQCCs of  $^2\text{H}$  and  $^{11}\text{B}$  nuclei, for the unit cell of original  $\text{NaBH}_4$  nanocrystal as well as other pressure-induced modified structures, are used to explore the electronic structures and steric factors that can control the B-H bonds strength.

## COMPUTATIONAL DETAILS

Initial geometries (Figs. 1-3) have been selected using experimentally-established nanocrystal structure data for  $\alpha$ -,  $\beta$ - and  $\gamma$ - $\text{NaBH}_4$  [17-20]. The structural parameters have been presented in Table 1. DFT calculations, well-proven for molecular calculations of  $\text{NaBH}_4$  [21], were performed using B3LYP computational method [22,23] and 6-311G\* basis set, implemented in the Gaussian software package [24], have been used for calculating and comparing the  $^2\text{H}$  and  $^{11}\text{B}$  NQCC parameters.

## RESULTS AND DISCUSSION

### Evaluations of NQCCs

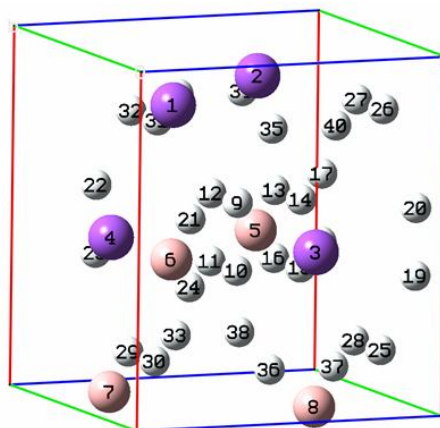
The formulation details for evaluating of NQR parameters have been reported elsewhere [15]. Briefly, the EFG is a traceless symmetric second-rank tensor. The principal tensor components are usually denoted as  $q_{zz}$ ,  $q_{yy}$  and  $q_{xx}$  in order of decreasing modulus; ( $eq_{ij} = \partial^2 V / \partial i \partial j$ ), where,  $i, j = X, Y, Z$ ;  $e$  is electron charge and  $V$  is the external electronic potential [14]. The expression  $\chi = e^2 Q q_{zz} / h$  is termed the NQCC and has the unit of frequency, Hertz (Hz);  $h$  is the Planck's constant, and  $Q$  is the nuclear electric quadrupole moment, and  $\chi$  is a measure of the interaction of the nuclear quadrupole moment with the molecular EFG tensor.

According to the previous studies [12,25,26], the nuclear electric quadrupole moments can be considered as simple constant (or scaling parameter), and, hence, are not parameterized. Among the wide range of standard values of quadrupole moments presented in literature, we selected  $Q(^2\text{H}) = 2.86 \text{ mb}$  and  $Q(^{11}\text{B}) = 40.59 \text{ mb}$  that have been reported by Pyykko [27]. It is evident that since the bond properties depend on electrons, no structural changes occur by replacing the hydrogen atoms by deuterium.

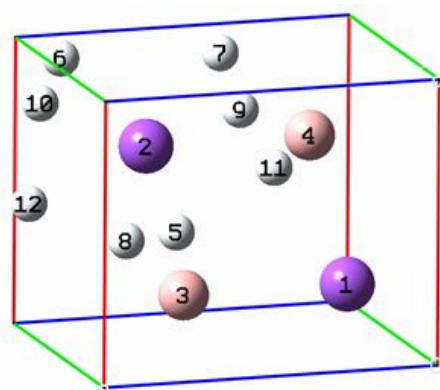
At ambient conditions,  $\text{NaBH}_4$  crystallizes in a cubic structure while Na atoms are located at 4a positions (0, 0, 0), B at 4b positions (0.5, 0.5, 0.5) and H at 32f sites with  $x = 0.3901$ . The octahedral arrangement of  $\text{BH}_4$  is surrounded by the alkali atoms.

Experimental results show the pressure-induced structural transitions of  $\alpha$ - $\text{NaBH}_4$  (cubic- $Fm\bar{3}m$ ) to  $\beta$ - $\text{NaBH}_4$  (tetragonal- $P4_21c$ ) at 6.3 GPa and further to an orthorhombic phase ( $Pnma$ ) and  $\gamma$ - $\text{NaBH}_4$  at 8.9 GPa [17]. The high-pressure orthorhombic phase found to be stable up to 30 GPa. It has been shown that by releasing the pressure back, the cubic phase is completely recovered.

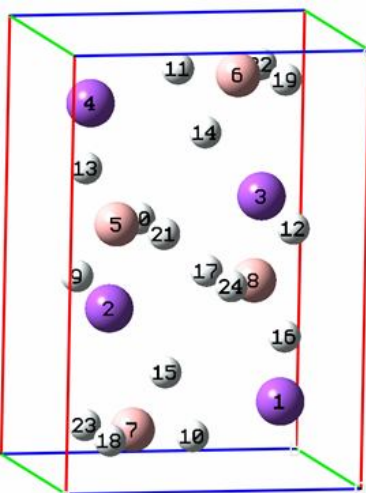
As mentioned before, in order to improve the hydrogen storage properties of sodium borohydride compounds, understanding the structural stability and bond nature of  $\text{NaBH}_4$  nanocrystals is essential. In the case of covalent bond formation between two different atoms, the shared electrons are not attracted equally by the two nuclei of



**Fig. 1.** Crystal structure of  $\alpha$ -NaBH<sub>4</sub>; the smallest circles are hydrogen atoms.



**Fig. 2.** Crystal structure of  $\beta$ -NaBH<sub>4</sub>; the smallest circles are hydrogen atoms.



**Fig. 3.** Crystal structure of  $\gamma$ -NaBH<sub>4</sub>; the smallest circles are hydrogen atoms.

**Table 1.** Experimental Structural Parameters for NaBH<sub>4</sub> Nanocrystals in Ambient and High-pressure Phases<sup>a</sup>

Phase	Unit-cell dimensions (Å)	Atom coordinates
$\alpha$ -NaBH <sub>4</sub> ( <i>fm3m</i> )	a = 6.150	Na: 0,0,0
		B: 0.5, 0.5,0.5
		H: 0.3901, 0.3901, 0.3901
$\beta$ -NaBH <sub>4</sub> ( <i>p42<sub>1</sub>c</i> )	a = 4.086	Na: 0, 0, 0
	c = 5.597	B: 0, 0, 0.5
		H: 0.069, 0.778, 0.340
$\gamma$ -NaBH <sub>4</sub> ( <i>pnma</i> )	a = 7.297	Na: 0.154, 0.25, 0.211
	b = 4.117	B: 0.592, 0.25, 0.784
	c = 5.569	H1: 0.468, 0.25, 0.916
		H2: 0.730, 0.25, 0.893
		H3: 0.414, 0.983, 0.336

<sup>a</sup>Ref. [17], [19], [20].

bonding atoms and hence we are deal with partial charges at two ends of the molecule. Unequal distribution of the electron cloud causes the polarity and partial ionic character. The percentage of partial ionic character depends upon the difference in electronegativity of the two atoms involved in covalent bond.

NaBH<sub>4</sub> is an ionic compound comprised of Na<sup>+</sup> and BH<sub>4</sub><sup>-</sup>. It is a great source of hydride ions. With B being positive and H being negative, the B-H bond is very polarized. In order to form a bond, the electrical charge should be transferred from the boron atom to the hydrogen atom. To have a strong binding interaction, the charge transfer mentioned should be significant, and larger <sup>2</sup>H-NQCC or smaller <sup>11</sup>B-NQCC is a criterion for the stronger B-H bond. From expression  $\chi = e^2 Q q_{zz} / h$ , it is obvious that NQCC of the nuclei is directly proportional to  $q_{zz}$ . Subsequently, increasing the charge density leads to increment of  $q_{zz}$ , and, hence, to the larger NQCC.

As shown in previous investigations [12,25-26], the NQCC's parameters are sensitive indicators for charge

distribution, and, hence, the interatomic bond strength. Subsequently, one can obtain the detailed inferences about the extent of electron transfer using the NQR data of the nucleus. In the present research, the B-H bond strength in normal and modified NaBH<sub>4</sub> unit cells has been investigated using the calculated NQCCs. The results are presented in Table 2.

According to the results, the calculated <sup>2</sup>H-NQCCs for  $\beta$ -NaBH<sub>4</sub> are smaller than those of other NaBH<sub>4</sub> phases ( $\alpha$ -NaBH<sub>4</sub> and  $\gamma$ -NaBH<sub>4</sub>). Hydrogen atoms with low-charge densities have smaller <sup>2</sup>H-NQCCs. Moreover, the average of <sup>11</sup>B-NQCCs in  $\beta$ -NaBH<sub>4</sub> is about 1-2 MHz greater than that of other studied phases. These observations (smaller <sup>2</sup>H-NQCCs and greater <sup>11</sup>B-NQCCs) confirm that B-H bonds in  $\beta$ -NaBH<sub>4</sub> nanocrystal are weaker than those in the other phases and the minimum charge transfer from B to H atoms is related to the  $\beta$ -phase.

B-H distances of  $\alpha$ -,  $\beta$ - and  $\gamma$ - NaBH<sub>4</sub>, are 1.17 Å, 1.30 Å and 1.17 Å, respectively, from synchrotron powder diffraction data [20]. This indicates weaker B-H bond in  $\beta$ -

**Table 2.** NQCCs of <sup>2</sup>H ( $\chi_H$ , kHz) and <sup>11</sup>B ( $\chi_B$ , MHz) in Unit Cells under Study, Calculated at the BLYP/6-311G\* Level

$\alpha$ -NaBH <sub>4</sub>		$\beta$ -NaBH <sub>4</sub>		$\gamma$ -NaBH <sub>4</sub>	
Hydrogen	$\chi_H$ (KHz)	Hydrogen	$\chi_H$ (KHz)	Hydrogen	$\chi_H$ (KHz)
H9	146.51	H7	9.30	H9	141.13
H11	151.85	H8	71.88	H11	128.92
H13	153.94	H9	86.82	H12	141.13
H15	151.85	H11	96.29	H13	128.92
H21	160.00			H14	123.09
H24	162.65			H15	123.09
H29	165.82			H16	128.92
H30	163.66			H17	172.06
H36	163.66			H18	165.45
H37	165.82			H19	166.79
				H20	166.13
				H21	172.06
				H22	165.45
				H23	166.79
				H24	166.13
Averaged calculated <sup>11</sup> B-NQCC (MHz)					
$\chi_B$ (MHz)		$\chi_B$ (MHz)		$\chi_B$ (MHz)	
5.54		6.60		4.31	

**Table 3.** *I*, *A* and Electrodonating Index ( $\omega^-$ ), in eV, of the Studied NaBH<sub>4</sub> Phases, at the B3LYP/6-311G\* Level

Studied phases	<i>I</i>	<i>A</i>	$\omega^-$
$\alpha$ -NaBH <sub>4</sub>	0.16458	0.14342	0.64
$\beta$ -NaBH <sub>4</sub>	0.19038	0.16704	0.78
$\gamma$ -NaBH <sub>4</sub>	0.18709	0.08629	0.17

NaBH<sub>4</sub> nanocrystal in agreement with NQCC results. Therefore, in β-NaBH<sub>4</sub> nanocrystal, hydrogens bind more weakly to the boron atom. It is expected that in the β-NaBH<sub>4</sub> phase, hydrogen atoms can be removed more easily and the β- phase can be considered as a promising candidate for being used as hydrogen storage material. In other words, NaBH<sub>4</sub>, at 6.3 GPa has a better condition for using as a hydrogen storage material.

### HOMO-LUMO Analysis

First principle calculations suggest that BH<sup>+</sup> ions decompose at the surface of NaBH<sub>4</sub> into H<sup>-</sup> ions and BH<sub>3</sub> molecules [28]. Dehydrogenation mechanism of complex metal hydrides is described on the basis of the interaction between negatively charged hydrogen of complex metal hydrides (H<sup>-</sup>, electron donor) and positively charged hydrogens of catalysts (H<sup>σ+</sup>, electron acceptor) [29]. Therefore, in studied phases, electrodonating index ( $\omega^-$ ) can be considered as a determining criterion for easier dehydrogenation.

The electrodonating  $\omega^-$  index is a suitable tool for the study of the reactivity of molecules, where  $\omega^-$  represents a measure of the propensity of a given system to donate electron density.

The highest occupied molecular orbital (HOMO) and the lowest un-occupied molecular orbital (LUMO) are very important parameters for quantum chemistry. The HOMO-LUMO energy calculations were carried out at the B3LYP/6-311G\* level of theory and the electrodonating index  $\omega^-$  of studied phases were calculated by the expression [31]:

$$\omega^- = \frac{I^2}{2(I - A)}$$

where  $I$  and  $A$  are  $-E_{\text{HOMO}}$  and  $-E_{\text{LUMO}}$ , respectively.

The results have been summarized in Table 3. As it is clear from the results, β-NaBH<sub>4</sub> has the highest electrodonating index corresponding to the easier condition for dehydrogenation in agreement with the results of NQCCs.

### NBO Analysis

In the next step, we applied natural bond orbital (NBO)

analysis for further analysis of hydrogen releasing in different NaBH<sub>4</sub> phases. NBO analysis provides an efficient way for investigation of reactivity and conjugative interactions in molecular systems [30]. The NBO calculations were carried out at the B3LYP/6-311G\* level of theory. To get a picture of the delocalization of electrons in B-H bonds of the studied nanocrystals, we have included calculations of the second order perturbation energy  $E(2)$  of the occupied NBO(i) of an electron donor which interact with the unoccupied NBO(j) of an electron acceptor. According to the analysis, the stabilization energy  $E(2)$  is given by the expression:

$$E(2) = \Delta E_{ij} = q_i \frac{F_{ij}^2}{\varepsilon_i - \varepsilon_j}$$

$q_i$  is the natural population of the donor NBO(i),  $F_{ij}$  is an off-diagonal element of the Fock matrix in NBO basis, and  $\varepsilon_i$  and  $\varepsilon_j$  are the donor and acceptor NBOs' energies. Table 4 lists the most relevant interacting orbitals that lead to loss of occupancy from the localized B-H NBOs of the studied structures.

In α-NaBH<sub>4</sub>, overall interaction of  $\sigma_{\text{B-H}}$  with the adjacent  $\sigma_{\text{B-H}}^*$  is 13.65 kcal mol<sup>-1</sup>. In β-NaBH<sub>4</sub> and γ-NaBH<sub>4</sub>, overall interaction of  $\sigma_{\text{B-H}}$  with adjacent  $\sigma_{\text{B-H}}^*$  is 32.47 and 20.82 kcal mol<sup>-1</sup>, respectively. These interactions are observed as an increase in electron density in B-H antibonding orbital that weaken the respective bonds [32]. In β-NaBH<sub>4</sub>, these interactions are greater than those of the other studied phases. As seen in Table 4, the strongest interaction in these nanocrystals is identified for the interaction of  $\sigma_{\text{B-H}}$  with the adjacent NBO lone pair orbital localized on Na in β-NaBH<sub>4</sub>;  $E(2) = 86.70$  kcal mol<sup>-1</sup>. The largest value of this interaction in β-NaBH<sub>4</sub> indicates more charge shift from B-H bond to Na lone pair, and, therefore, more destabilizing for B-H bond compared to the other considered nanocrystals.

NBO results verify that the mentioned interactions have weakened B-H bond in the β-NaBH<sub>4</sub> phase compared to other phases, and, thus hydrogen releasing in this phase is easier than that in α- and γ-NaBH<sub>4</sub>.

It was also observed from the NBO analysis that only the ambient phase (α-NaBH<sub>4</sub>) has a strong Na-B bond with high ionic character and this NBO is more polarized towards B (Table 5).

**Table 4.** Donor and Acceptor NBOs of the Studied NaBH<sub>4</sub> Phases

Interaction (donor→acceptor)	E(2) (Kcal mol <sup>-1</sup> )
$\alpha$ -NaBH <sub>4</sub>	
$\sigma$ B6 - H21 → $\sigma^*$ B6 - H24	1.56
$\sigma$ B6 - H24 → $\sigma^*$ B6 - H21	2.66
$\sigma$ B5 - H9 → $\sigma^*$ B5 - H9	2.49
$\sigma$ B5 - H11 → $\sigma^*$ B5 - H11	2.15
$\sigma$ B5 - H13 → $\sigma^*$ B5 - H13	5.64
$\sigma$ B5 - H15 → $\sigma^*$ B 5 - H15	2.15
$\sigma$ B6 - H21 → LP*Na1	0.67
$\sigma$ B6 - H21 → LP*Na3	4.19
$\sigma$ B6 - H24 → LP*Na3	3.34
$\sigma$ B6 - H21 → LP*Na 4	4.19
$\sigma$ B6 - H24 → LP*Na 4	3.34
$\beta$ -NaBH <sub>4</sub>	
$\sigma$ B4 - H7 → $\sigma^*$ B4 - H7	2.51
$\sigma$ B4 - H7 → $\sigma^*$ B4 - H9	8.81
$\sigma$ B4 - H7 → $\sigma^*$ B4 - H1 1	9.58
$\sigma$ B4 - H9 → $\sigma^*$ B4 -H7	2.34
$\sigma$ B4 - H9 → $\sigma^*$ B4 - H1 1	2.01
$\sigma$ B4 - H11 → $\sigma^*$ B4 - H7	4.78
$\sigma$ B4 - H11 → $\sigma^*$ B4 - H9	2.44
$\sigma$ B3 - H8 → LP*Na2	13.73
$\sigma$ B4 - H7 → LP*Na1	9.55
$\sigma$ B4 - H7 → LP*Na2	86.70
$\sigma$ B4 - H9 → LP*Na2	15.64
$\sigma$ B4 - H11 → LP*Na2	20.49
$\sigma$ B4 - H7 → LP* B4	0.72
$\sigma$ B4 - H9 → LP*B4	0.86
$\sigma$ B4 - H11 → LP* B4	0.57
$\gamma$ -NaBH <sub>4</sub>	
$\sigma$ B6 - H11 → $\sigma^*$ B 6 - H14	2.50
$\sigma$ B6 - H11 → $\sigma^*$ B6 - H19	1.19
$\sigma$ B6 - H14 → $\sigma^*$ B6 - H11	3.67
$\sigma$ B6 - H19 → $\sigma^*$ B6 - H11	1.93
$\sigma$ B6 - H22 → $\sigma^*$ B 6 - H11	1.12
$\sigma$ B7 - H10 → $\sigma^*$ B 7 - H15	2.50
$\sigma$ B7 - H10 → $\sigma^*$ B 7 - H23	1.19
$\sigma$ B7 - H15 → $\sigma^*$ B 7 - H10	3.67
$\sigma$ B7 - H18 → $\sigma^*$ B 7 - H10	1.12
$\sigma$ B7 - H23 → $\sigma^*$ B 7 - H10	1.93
$\sigma$ B5 - H9 → LP*Na2	3.13
$\sigma$ B5 - H20 → LP*Na2	19.77
$\sigma$ B5 - H21 → LP*Na3	7.12
$\sigma$ B6 - H11 → LP*Na 4	32.67
$\sigma$ B6 - H14 → LP*Na 4	1.94
$\sigma$ B7 - H10 → LP*Na1	47.08

**Table 5.** Polarization Coefficients and Ionic Character of Na-B Bond in the Studied NaBH<sub>4</sub> Phases

	$\alpha$ -NaBH <sub>4</sub>	$\beta$ -NaBH <sub>4</sub>	$\gamma$ -NaBH <sub>4</sub>
$C_{Na}^*$	0.2893	-	-
$C_B^*$	0.9572	-	-
$i_{NaB}$	0.85	-	-

Using NBO analysis, the polarization coefficients of Na ( $C_{Na}^* = 0.2893$ ) and B ( $C_B^* = 0.9572$ ) in  $\alpha$ -NaBH<sub>4</sub> were obtained and the ionic character of Na-B bonds ( $i_{NaB} = 0.85$ ) were calculated by [31]:

$$i_{NaB} = \frac{C_B^{*2} - C_{Na}^{*2}}{C_B^{*2} + C_{Na}^{*2}}$$

However, this bond (Na-B) was not found in pressure induced phases ( $\beta$ -NaBH<sub>4</sub> and  $\gamma$ -NaBH<sub>4</sub>). In other words, due to strong ionic bonding nature, dissociation temperatures of  $\alpha$ -NaBH<sub>4</sub> are very high and the stability of  $\alpha$ -NaBH<sub>4</sub> decreases with pressure increasing.

## CONCLUSIONS

In the present research, we have studied the normal ( $\alpha$ -NaBH<sub>4</sub>) and modified forms (high-pressure phases;  $\beta$ -NaBH<sub>4</sub> and  $\gamma$ -NaBH<sub>4</sub>) of sodium borohydride. NQR spectroscopy has been applied to obtain the NQCCs to explain the charge distribution and the strength of B-H bonds. Our results show the smaller value of <sup>2</sup>H-NQCCs and higher value of <sup>11</sup>B-NQCCs for  $\beta$ -NaBH<sub>4</sub> compared to other phases indicating the weaker B-H bonds in  $\beta$ -phase. Subsequently, dehydrogenation is more feasible for this modified phase, and, hence,  $\beta$ -NaBH<sub>4</sub> can be considered as a promising candidate for the use as a hydrogen storage material. Based on the HOMO-LUMO analysis, in agreement with NQR spectroscopy calculations, dehydrogenation is more feasible in  $\beta$ -phase due to more propensity of this phase to donate electron density than the other phases considered, and, therefore  $\beta$ -NaBH<sub>4</sub> can be

considered as a good candidate for being used as a hydrogen storage material. NBO results indicate that some interactions produce greater loss of occupancy in the localized B-H NBOs of  $\beta$ -NaBH<sub>4</sub> compared to B-H bonds in other studied phases that weakens the respective bonds in accordance to NQCC results.

## ACKNOWLEDGEMENTS

This research is financially supported by Payame Noor University, Tehran.

## REFERENCES

- [1] Muir, S. S.; Yao, X. D., Progress in sodium borohydride as a hydrogen storage material: Development of hydrolysis catalysts and reaction systems. *Int. J. Hydrogen Energy*, **2011**, *36*, 5983-5997, DOI: 10.1016/j.ijhydene.2011.02.032.
- [2] Mao, J.; Gregory, D. H., Recent advances in the use of sodium borohydride as a solid state hydrogen store. *Energies*, **2015**, *8*, 430-453; DOI: 10.3390/en8010430.
- [3] Bertheville, B.; Fischer, P.; Yvon, K., High-pressure synthesis and crystal structures of new ternary caesium magnesium hydrides, CsMgH<sub>3</sub>, Cs<sub>4</sub>Mg<sub>3</sub>H<sub>10</sub> and Cs<sub>2</sub>MgH<sub>4</sub>. *J. Alloys Compd.* **2002**, *330-332*, 152-156, DOI: 10.1016/S0925-8388(01)01631-0.
- [4] Ronnebro, E.; Kitamura, N.; Skai, T., The gigapascal pressure thermal technique for synthesising new ternary metal hydrides in the A-Pd-H (A = Li, Na or Mg) system. *J. Alloys Compd.*



- 2003, 358, 216-222, DOI: 10.1016/S0925-8388(03)00042-2.
- [5] Felderhoff, M.; Weidenthaler, C.; von Helmolt, R.; Eberle, U., Hydrogen storage: the remaining scientific and technological challenges. *Phys. Chem. Chem. Phys.* **2007**, 9, 2643-2653, DOI: 10.1039/B701563C.
- [6] Urganani, J.; Torres, F.; Palumbo, M.; Baricco, M., Hydrogen release from solid state NaBH<sub>4</sub>. *Int. J. Hydrogen Energy* **2008**, 33, 3111-3115, DOI: 10.1016/j.ijhydene.2008.03.031
- [7] Grochala, W.; Edwards, P., Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen. *Chem. Rev.* **2004**, 104, 1283-1315, DOI: 10.1021/cr030691s.
- [8] Demirci, U. B.; Akdim, O.; Miele, P., Ten-year efforts and a no-go recommendation for sodium borohydride for on-board automotive hydrogen storage. *Int. J. Hydrogen Energy*, **2009**, 34, 2638-2345, DOI: 10.1016/j.ijhydene.2009.01.038.
- [9] Liu, B. H.; Li, Q., A highly active Co-B catalyst for hydrogen generation from sodium borohydride hydrolysis. *Int. J. Hydrogen Energy*, **2008**, 33, 7385-7391, DOI: 10.1016/j.ijhydene.2008.09.055.
- [10] Huang, Y.; Wang, Y.; Zhao, R.; Shen, P. K.; Wei, Z., Accurately measuring the hydrogen generation rate for hydrolysis of sodium borohydride on multiwalled carbon nanotubes/Co-B catalysts. *Int. J. Hydrogen Energy*, **2008**, 33, 7110-7115, DOI: 10.1016/j.ijhydene.2008.09.046.
- [11] Blomqvist, H.; Ronnebro, E.; Kyoji, D.; Sakai, T.; Noreus, D., Structural characterization of Mg<sub>3</sub>MnH<sub>6</sub>-a new high-pressure phase synthesized in a multi-anvil cell at 6GPa. *J. Alloy. Compd.* **2003**, 358, 82-86, DOI: 10.1016/S0925-8388(03)00127-0.
- [12] Rafiee, M. A., A theoretical study of MgH<sub>2</sub> ambient and high pressure phases using NQCC parameters. *Russ. J. Phys. Chem. A* **2014**, 88, 2359-2362, DOI: 10.1134/S0036024414130172.
- [13] Leach, A. R., Molecular Modeling Principles and Applications. Longman, Singapore Publishers, Singapore, 1997, Chap. 5.
- [14] Lucken, E. A. C., Nuclear Quadrupole Coupling Constants. Academic Press, London, 1969, Chap., 1-4.
- [15] Graybeal, J. D., Molecular spectroscopy. McGraw Hill, Singapore, 1988, Chap. 10
- [16] Slichter, C. P. Principles of Magnetic Resonance. Springer-verlag, New York, 1992, Chap. 10.
- [17] Kumar, R. S.; Cornelius, A. L., Structural transitions in NaBH<sub>4</sub> under pressure. *Appl. Phys. Lett.* **2005**, 87, 261916, DOI: 10.1063/1.2158505.
- [18] Johnston, H. J.; Hallett, N. C., Low temperature heat capacities of inorganic solids. XIV. Heat capacity of sodium borohydride from 15-300°K. *J. Am. Chem. Soc.* **1953**, 75, 1467-1468, DOI: 10.1021/ja01102a056.
- [19] Kim, E.; Kumar, R.; Weck, P. F.; Cornelius, A. L.; Nicol, M.; Vogel, S. C.; Zhang, J. Z.; Hartl, M.; Stowe, C.; Daemen, L.; Zhao, Y. S., Pressure-driven phase transitions in NaBH<sub>4</sub>: theory and experiments. *J. Phys. Chem. B* 2007, 111, 13873-13876, DOI: 10.1021/jp709840w
- [20] Filinchuk, Y.; Talyzin, A. V.; Chernyshov, D.; Dmitriev, V., High-pressure phase of NaBH<sub>4</sub>: Crystal structure from synchrotron powder diffraction data. *Phys. Rev. B* **2007**, 76, 092104, DOI: 10.1103/PhysRevB.76.092104.
- [21] Zyubin, A. S.; Zyubina, T. S.; Kravchenko, O. V.; Solov'ev, M. V.; Dobrovolskii, Y. A., Quantum-chemical modeling of dehydrogenation of a sodium borohydride molecule in water, *Russ. J. Inorg. Chem.*, **2016**, 61, 731-739, DOI: 10.1134/S0036023616060231.
- [22] Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* **1993**, 98, 5648-52, DOI: 10.1063/1.464913.
- [23] Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*, **1988**, 37, 785-789, DOI: 10.1103/PhysRevB.37.785.
- [24] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E. Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.;

- Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; & Pople, J. A., GAUSSIAN 09, 2003, Pittsburgh, PA: Gaussian Inc.
- [25] Rafiee, M. A.; Partoee, T., Investigation of the binding affinity between styrylquinoline inhibitors and HIV integrase using calculated nuclear quadrupole coupling constant (NQCC) parameters (A theoretical ab initio study). *Bull. Korean Chem. Soc.* **2011**, *32*, 208-212, DOI: 10.5012/bkcs.2011.32.1.208.
- [26] Rafiee, M. A., Comparison of metal additives and Boron atom on MgH<sub>2</sub> absorbing-desorbing characteristics using calculated NQCCs. *Int. J. Nano Dimens.* **2015**, *6*, 289-295.
- [27] Pyykko, P., Spectroscopic nuclear quadrupole moments. *Mol. Phys.* **2001**, *99*, 1617-1629, DOI: 10.1080/00268970110069010.
- [28] Cakır, D.; Wijs, G. A. D.; Brocks, G., Native defects and the dehydrogenation of NaBH<sub>4</sub>. *J. Phys. Chem. C*, **2011**, *115*, 24429-24434, DOI: 10.1021/jp208642g.
- [29] Lu, J.; Fang, Z. Z.; Sohn, H. Y., A dehydrogenation mechanism of metal hydrides based on interactions between H<sup>δ+</sup> and H<sup>-</sup>, *Inorg. Chem.*, **2006**, *45*, 8749-8754, DOI: 10.1021/ic060836o.
- [30] Weinhold, F.; Landis, C. R., Natural bond orbitals and extensions of localized bonding concepts. *Chem. Educ. Res. Pract.* **2001**, *2*, 91-104, DOI: 10.1039/B1RP90011K.
- [31] Domingo, L. R.; Ríos-Gutiérrez, M.; Pérez, P., Applications of the conceptual density functional theory indices to organic chemistry reactivity, *Molecules*, **2016**, *21*, 748-760; DOI: 10.3390/molecules21060748.
- [32] Sebastian, S.; Sundaraganesan, N., The spectroscopic (FT-IR, FT-IR gas phase, FT-Raman and UV) and NBO analysis of 4-Hydroxypiperidine by density functional method, *Spectrochimica Acta A*, **2010**, *75*, 941-952; DOI: 10.1016/j.saa.2009.11.030