

Study of Dehydrogenation of Pressure-induced NaBH₄ Structures Using Calculated NQCC Parameters

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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, NaBH₄, 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 NaBH₄ in fuel cells. One way to overcome this problem is applying the high-pressure techniques and using the pressure-induced NaBH₄ structures. Under ambient conditions, NaBH₄ has a cubic structure (α -NaBH₄) that can be converted to β - and γ -NaBH₄ by increasing the pressure. In the present research, charge distribution of α -NaBH₄ nanocrystal has been compared to that of high-pressure structures using calculated NQCCs to study the effect of pressure on different NaBH₄ structures and their hydrogen desorption ability. Our results show the smaller value of ²H-NQCCs and higher value of ¹¹B-NQCCs for β -NaBH₄ respect to other structures. In other words, the B-H bond is weaker in β -NaBH₄, and it is expected that dehydrogenation occurs more feasible at lower temperatures in β -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 (NaBH₄), 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 (NaBH₄) 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 (MAIH₄; 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 NaBH₄ and other M-BH₄ (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 NaBH₄ 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 NaBH₄. 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

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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 ^2H and ^{11}B nuclei, for the unit cell of original 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 α -, β - and γ - NaBH_4 [17-20]. The structural parameters have been presented in Table 1. DFT calculations, well-proven for molecular calculations of 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 ^2H and ^{11}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 χ 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, 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 BH_4 is surrounded by the alkali atoms.

Experimental results show the pressure-induced structural transitions of α - NaBH_4 (cubic- $Fm\bar{3}m$) to β - NaBH_4 (tetragonal- $P4_21c$) at 6.3 GPa and further to an orthorhombic phase ($Pnma$) and γ - 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 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

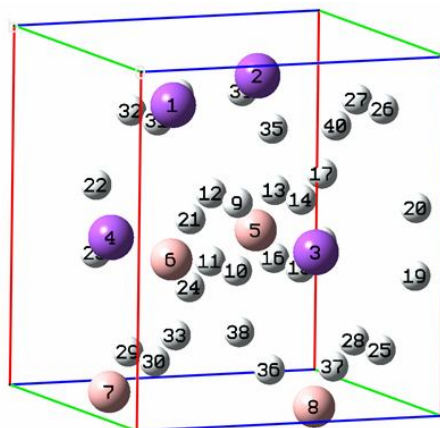


Fig. 1. Crystal structure of α -NaBH₄; the smallest circles are hydrogen atoms.

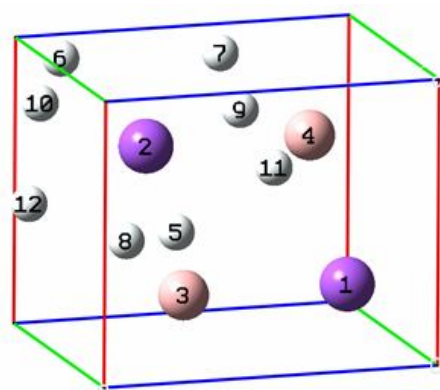


Fig. 2. Crystal structure of β -NaBH₄; the smallest circles are hydrogen atoms.

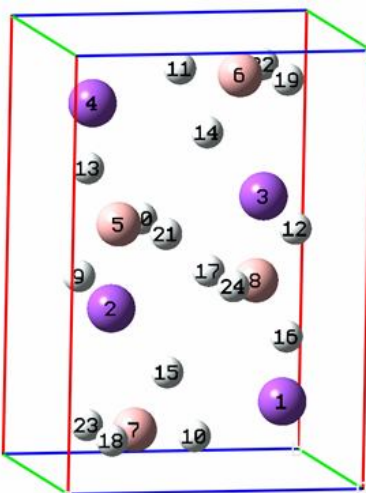


Fig. 3. Crystal structure of γ -NaBH₄; the smallest circles are hydrogen atoms.

Table 1. Experimental Structural Parameters for NaBH₄ Nanocrystals in Ambient and High-pressure Phases^a

Phase	Unit-cell dimensions (Å)	Atom coordinates
α -NaBH ₄ (<i>fm3m</i>)	a = 6.150	Na: 0,0,0
		B: 0.5, 0.5,0.5
		H: 0.3901, 0.3901, 0.3901
β -NaBH ₄ (<i>p42₁c</i>)	a = 4.086	Na: 0, 0, 0
	c = 5.597	B: 0, 0, 0.5
		H: 0.069, 0.778, 0.340
γ -NaBH ₄ (<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

^aRef. [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.

NaBH₄ is an ionic compound comprised of Na⁺ and BH₄⁻. 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 ²H-NQCC or smaller ¹¹B-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 NaBH₄ unit cells has been investigated using the calculated NQCCs. The results are presented in Table 2.

According to the results, the calculated ²H-NQCCs for β -NaBH₄ are smaller than those of other NaBH₄ phases (α -NaBH₄ and γ -NaBH₄). Hydrogen atoms with low-charge densities have smaller ²H-NQCCs. Moreover, the average of ¹¹B-NQCCs in β -NaBH₄ is about 1-2 MHz greater than that of other studied phases. These observations (smaller ²H-NQCCs and greater ¹¹B-NQCCs) confirm that B-H bonds in β -NaBH₄ nanocrystal are weaker than those in the other phases and the minimum charge transfer from B to H atoms is related to the β -phase.

B-H distances of α -, β - and γ - NaBH₄, 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 β -

Table 2. NQCCs of ²H (χ_H , kHz) and ¹¹B (χ_B , MHz) in Unit Cells under Study, Calculated at the BLYP/6-311G* Level

α -NaBH ₄		β -NaBH ₄		γ -NaBH ₄	
Hydrogen	χ_H (KHz)	Hydrogen	χ_H (KHz)	Hydrogen	χ_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 ¹¹ B-NQCC (MHz)					
χ_B (MHz)		χ_B (MHz)		χ_B (MHz)	
5.54		6.60		4.31	

Table 3. *I*, *A* and Electrodonating Index (ω^-), in eV, of the Studied NaBH₄ Phases, at the B3LYP/6-311G* Level

Studied phases	<i>I</i>	<i>A</i>	ω^-
α -NaBH ₄	0.16458	0.14342	0.64
β -NaBH ₄	0.19038	0.16704	0.78
γ -NaBH ₄	0.18709	0.08629	0.17

NaBH₄ nanocrystal in agreement with NQCC results. Therefore, in β-NaBH₄ nanocrystal, hydrogens bind more weakly to the boron atom. It is expected that in the β-NaBH₄ 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, NaBH₄, at 6.3 GPa has a better condition for using as a hydrogen storage material.

HOMO-LUMO Analysis

First principle calculations suggest that BH⁺ ions decompose at the surface of NaBH₄ into H⁻ ions and BH₃ 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⁻, electron donor) and positively charged hydrogens of catalysts (H^{σ+}, electron acceptor) [29]. Therefore, in studied phases, electrodonating index (ω^-) can be considered as a determining criterion for easier dehydrogenation.

The electrodonating ω^- index is a suitable tool for the study of the reactivity of molecules, where ω^- 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 ω^- 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-NaBH₄ 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 NaBH₄ 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 ε_i and ε_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-NaBH₄, overall interaction of $\sigma_{\text{B-H}}$ with the adjacent $\sigma_{\text{B-H}}^*$ is 13.65 kcal mol⁻¹. In β-NaBH₄ and γ-NaBH₄, overall interaction of $\sigma_{\text{B-H}}$ with adjacent $\sigma_{\text{B-H}}^*$ is 32.47 and 20.82 kcal mol⁻¹, respectively. These interactions are observed as an increase in electron density in B-H antibonding orbital that weaken the respective bonds [32]. In β-NaBH₄, 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-NaBH₄; $E(2) = 86.70$ kcal mol⁻¹. The largest value of this interaction in β-NaBH₄ 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-NaBH₄ phase compared to other phases, and, thus hydrogen releasing in this phase is easier than that in α- and γ-NaBH₄.

It was also observed from the NBO analysis that only the ambient phase (α-NaBH₄) 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 NaBH₄ Phases

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

Table 5. Polarization Coefficients and Ionic Character of Na-B Bond in the Studied NaBH₄ Phases

	α -NaBH ₄	β -NaBH ₄	γ -NaBH ₄
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 α -NaBH₄ 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 (β -NaBH₄ and γ -NaBH₄). In other words, due to strong ionic bonding nature, dissociation temperatures of α -NaBH₄ are very high and the stability of α -NaBH₄ decreases with pressure increasing.

CONCLUSIONS

In the present research, we have studied the normal (α -NaBH₄) and modified forms (high-pressure phases; β -NaBH₄ and γ -NaBH₄) 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 ²H-NQCCs and higher value of ¹¹B-NQCCs for β -NaBH₄ compared to other phases indicating the weaker B-H bonds in β -phase. Subsequently, dehydrogenation is more feasible for this modified phase, and, hence, β -NaBH₄ 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 β -phase due to more propensity of this phase to donate electron density than the other phases considered, and, therefore β -NaBH₄ 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 β -NaBH₄ compared to B-H bonds in other studied phases that weakens the respective bonds in accordance to NQCC results.

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