A Theoretical Study of the Spectroscopic Properties of B_2H_6 and of a series of $B_xH_y^{z-}$ species ($x = 1 - 12$, $y = 3 - 14$, $z = 0 - 2$): from BH_3 to $B_{12}H_{12}^{2-}$

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Abstract

The characterization of boron-hydrogen compounds is an active research area which encompasses subjects as diverse as the chemistry and structures of closoboranes or the thermal decomposition mechanism of the borohydrides. Due to their high gravimetric hydrogen content, borohydrides are considered as potential hydrogen storage materials. Their thermal decompositions are multistep processes, for which the intermediate products are not easily identified. To help address this issue, we have extensively investigated the vibrational and NMR properties of 21 relevant $B_mH_n^{z-}$ boron-hydrogen species ($m = 1-12$; $n = 1-14$; $z = 0-2$) within density functional theory. We could thus show that the B3LYP-D2 dispersion-corrected hybrid can be used in combination with the large cc-pVTZ basis set for the reliable prediction of the ^{11}B and 1H NMR spectra of the boron-hydrogen species, and also for the reliable prediction of their IR and Raman spectra while taking into account the anharmonicity of their molecular vibrations.

Keywords: boron-hydrogen species; ^{11}B and 1H NMR chemical shifts; vibrational frequencies; anharmonicity; density functional theory

1. Introduction

Boron-hydrogen compounds attract a lot of interest for a variety of reasons. On one side, the chemistry and structures of closoboranes continues to be studied, as shown in the

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recent structural studies of $M_2B_7H_7$ and MB_7H_8 ($M = PPh_4$, PNP, and $N(n-Bu_4)$) [1, 2]. The chemistry of $B_3H_8^-$ has also been recently discussed in detail [3–7].

Many previous theoretical studies have addressed the structures and relative energies of different boron-hydrogen species [8–19]. These species can also behave as complexants. In this respect, quantum chemistry was recently applied to the design of the $Li@B_{10}H_{14}$ electride and to the study of its electronic and vibrational nonlinear optical properties [20–22]. Of most interest to us, metal borohydrides have been receiving considerable attention from both physicists and chemists because of their potential use as hydrogen storage materials [23]. These materials have high gravimetric hydrogen content [24, 25] which is suitable for mobile applications [25–28]. Their thermal decomposition leads to various intermediate compounds [7, 29–36] which are not easily identified. Moreover the thermal paths are complex and pass through many steps [27].

In this study, we performed DFT [37, 38] calculations on a series of $B_xH_y^{z-}$ compounds ($x = 1-12$; $y = 3-12, 14$; $z = 0-2$) from BH_3 to $B_{12}H_{12}^{2-}$ with the aim to obtain a consistent set of calculated vibrational and NMR spectroscopic data. The compound B_2H_6 is first studied in detail to choose the best practical theoretical method, which is capable of treating molecules as large as $B_{12}H_{12}^{2-}$ and which takes into account as much as possible the anharmonicity of their molecular vibrations. This method is then applied to all other compounds.

These data are critically compared to the available experimental data and are expected to allow, by a combined computational and experimental approach, the identification of intermediate species formed during the decomposition of borohydrides.

2. Computational Details

All calculations were performed using the Gaussian09 package [39]. For the benchmark study of B_2H_6 , DFT calculations were carried out with the B3LYP, [40, 41] PBE0 [42, 43] and M06-HF [44] functionals. The influence of dispersion correction was assessed by using the Grimme’s D2 [45], D3 [46] and D3BJ [47] correction schemes. *Ab initio* calculations were also performed with the Hartree-Fock, the second-order Møller-Plesset perturbation

theory (MP2) [48] and the CCSD(T) [49] methods. Several basis sets were employed for describing the B and H atoms: the 6-31G* [50, 51] Pople basis set of split valence polarized quality, the 6-311++G** [52, 53] Pople basis set of triple- ζ polarized quality augmented with diffuse functions, the Ahlrichs def2-TZVP [54] basis set of triple- ζ polarized quality, and the Dunning cc-pVTZ [55] correlation-consistent basis set. Several other Ahlrichs and Dunning basis sets of lesser or higher flexibility were also used to probe the influence of the basis sets. To ease the reading of the manuscript, the corresponding results are given as Supporting Information: the results obtained with the largest of these Ahlrichs (resp., Dunning) basis sets and with the aforementioned def2-TZVP (resp., cc-pVTZ) basis set are indeed very similar. The benchmark DFT calculations were extended to B_3H_8^- and the B3LYP-D2/cc-pVTZ method was used for the study of the remaining boron-hydrogen species.

The characterization of a species at a given theoretical level consisted first in the optimization of its geometry using an “ultrafine” grid of 99 radial shells and 590 angular points *per* shell and “tight” convergence criteria for the forces and displacements, which help ensure well converged calculated frequencies (see Supporting Information). Vibrational frequencies analyses are then conducted both in the harmonic and in the anharmonic approximation using second-order perturbation theory as implemented by Barone [56–58] in the Gaussian09 package. Using the optimized geometry, NMR chemical shifts are calculated with the Gauge-independent atomic orbital (GIAO) method [59] using $\text{BF}_3\cdot\text{OEt}_2$ [60] and tetramethylsilane (TMS) as references for ^{11}B and ^1H chemical shifts, respectively.

3. Results and Discussion

At first, the spectroscopic properties of B_2H_6 were calculated with different theoretical approaches in order to determine the best practical approach which is applicable for larger molecules (such as $\text{B}_{12}\text{H}_{12}^{2-}$) and to discuss the limits of this approach. Subsequently, this approach is applied systematically to all other compounds and the results compared with available literature data.

3.1. Diborane, B_2H_6

Diborane, B_2H_6 [61], is the simplest stable borohydride at ambient condition [62]. It has a ring-type molecular structure and has two-bridging hydrogens [63] (see Figure 1). Begue [64] used high-level calculations to investigate the anharmonic vibrational properties of this compound.

3.1.1. Structure of diborane

Diborane has one B–B, four terminal and two bridging B–H bonds as shown in Figure 1. It has D_{2h} symmetry. It has a planar ring which consists of two-bridging hydrogens and two boron atoms.

Figure 1: The structure of B_2H_6 .

Table 1 compares the experimental and calculated structural data for B_2H_6 . The experimental data were obtained from high-resolution infra-red spectroscopy (Exp. (IR)) [65] and from gas-phase electron diffraction (Exp. (GED)) [66]. The calculated values are in good agreement with experimental data. The B–H_{b(bridge)} bond is longer than the terminal B–H bond by ca. 0.1 Å. The structural parameters obtained with different levels of theory are comparable and show that the ring of diborane is planar with a H_b–B–H_b–B dihedral angle of 0 deg.

3.1.2. NMR chemical shifts of diborane

The calculated NMR chemical shifts of diborane are shown in Table 2. The calculated values of the ^{11}B chemical shifts are typically 1 to 2 ppm smaller than the experiment value. Using B3LYP and PBE0 with different types of basis sets give comparable results which are better than those obtained with MP2. The calculated NMR data will be discussed in more details below, taking into account all compounds which we have studied.

Table 1: Selected calculated and experimental structural parameters for B₂H₆: bond distances are given in Å and bond angles in deg

	B3LYP			PBE0	MP2
	6-311++G**	cc-pVTZ	def2-TZVP	cc-pVTZ	6-311++G**
B-B	1.764	1.758	1.758	1.747	1.768
B-H	1.186	1.185	1.186	1.190	1.188
B-H _b	1.315	1.312	1.312	1.314	1.316
H-B-H	121.7	121.7	121.6	121.7	122.3
H _b -B-H _b	95.8	95.8	95.8	96.7	95.6
B-H _b -B	84.2	84.2	84.2	83.3	84.4
H _b -B-H _b -B	0.0	0.0	0.0	0.0	0.0

	B3LYP-D2	B3LYP-D3BJ	CCSD(T)	Exp.	Exp.
	cc-pVTZ	cc-pVTZ	cc-pVTZ	(IR) ^a	(GED) ^b
B-B	1.764	1.757	1.763	1.743	1.747(7)
B-H	1.186	1.185	1.188	1.184(3)	1.182(11)
B-H _b	1.315	1.312	1.315	1.314(3)	1.303 (11)
H-B-H	121.8	121.7	122.3	121.5(5)	120.5
H _b -B-H _b	95.8	95.9	95.8	96.9(5)	95.9
B-H _b -B	84.2	84.1	84.2	-	-
H _b -B-H _b -B	0.0	0.0	47.9	-	-

^aRef. 65, ^bRef. 66

3.1.3. Vibrational spectroscopy of diborane

B₂H₆ has D_{2h} symmetry. Diborane has 18 vibrational modes. Its normal modes transform as $4A_g$, $3B_{1g}$, $3B_{2g}$, $2B_{3g}$, $1A_u$, $3B_{1u}$, $4B_{2u}$, and $4B_{3u}$. The A_g , B_{1g} , B_{2g} , and B_{3g} modes are Raman active while the B_{1u} , B_{2u} , B_{3u} modes are IR active, and the A_u mode is neither IR nor Raman active. The vibrational spectra of diborane and its isotopic analogs have been thoroughly studied by Duncan [68]. The combination of all experimental data allowed to estimate the harmonic frequencies for this molecule, which are also included in Table 3.

In Table 3, calculated PBE0/cc-pVTZ and B3LYP/cc-pVTZ harmonic and anharmonic frequencies are compared to the experimental values. Drawings of the corresponding modes are given in the Supplementary Materials. Modes ν_9 and ν_{10} correspond to the bending modes of the terminal BH₂ groups. Modes ν_{11} - ν_{14} are associated with motions of the bridging H atoms; and modes ν_{15} - ν_{18} are the stretching modes of the terminal BH₂ groups. The values

Table 2: Calculated ^{11}B NMR and ^1H chemical shifts of diborane (in ppm) relative to $\text{BF}_3\cdot\text{OEt}_2$ and TMS, respectively. Available experimental data are also given

Method	Calc. $\delta^{11}\text{B}$	$\text{H}_{\text{terminal}}$	H_{bridge}
MP2/6-31G*	12.2	4.32	-0.88
MP2/6-311++G**	14.1	4.27	-0.90
B3LYP/6-311++G**	15.0	4.57	-0.64
B3LYP/def2TZVP	15.6	4.57	-0.66
B3LYP/cc-pVTZ	15.1	4.45	-0.76
PBE0/cc-pVTZ	16.0	4.66	-0.60
Exp. ^a	16.6	-	-

^aRef. 67

of the harmonic low frequencies (ν_1 - ν_{10}) and of the terminal stretching modes correspond quite well to the experimental harmonic frequencies. However significant differences appear for the modes ν_{11} - ν_{14} . In order to improve the agreement, anharmonic calculations have been performed and are compared with the experimental anharmonic data in Table 3.

The inclusion of anharmonicity immediately led to an improvement of the calculated frequencies with respect to the experimental values. In order to evaluate the influence of the level of calculations, we have systematically varied the functionals, the basis sets and we also performed CCSD(T) calculations to obtain a benchmark reference. Different convergence criteria were tested and showed that using “**tight**” convergence criteria for the forces is necessary to obtain well converged frequencies (see Supporting Information). The results thus obtained are summarized in Table 4, which shows the RMS errors with respect to the experimental frequencies.

Inspection of Table 4 shows that both PBE0 and B3LYP give comparable results, with slightly better RMS values for PBE0 (using the same basis set). However, if one excludes the modes ν_{11} - ν_{14} from the RMS calculations (RMS* values in Table 4), it appears that B3LYP gives significantly better results for all other frequencies. Different basis sets were tested and show that better results are obtained using Dunning’s type (cc-pVTZ) and Ahlrich’s type (def2TZVP) basis sets. The lowest RMS*-value is found for B3LYP (cc-pVTZ). Finally, dispersion was considered. The use of the dispersion-corrected B3LYP-D2, -D3 and -D3BJ functionals does not have a significant influence on the predicted geometries (Table 1). However, the use of B3LYP-D2 led to the smallest RMS value of 27.2 cm^{-1} , compared to

Table 3: Calculated harmonic and anharmonic frequencies of B_2H_6 , and RMS errors with respect to experimental data (frequencies are in cm^{-1} ; the cc-pVTZ basis set was used for all calculations)

Mode	Symm	Harmonic		Empirical	Anharmonic			Exp. ^a
		PBE0	B3LYP	Harmonic ^a	PBE0	B3LYP	B3LYP-D2	
ν_1	B_{2u}	329	360	376	340	362	365	369
ν_2	A_g	821	801	798	787	766	774	790
ν_3	A_u	850	850	850	824	823	819	833
ν_4	B_{2g}	898	894	877	868	860	858	860
ν_5	B_{1g}	912	940	933	907	917	922	915
ν_6	B_{2u}	930	954	968	885	923	914	949
ν_7	B_{1u}	979	992	993	958	970	965	973
ν_8	B_{3g}	993	1022	1041	957	998	971	1020
ν_9	B_{3u}	1181	1197	1196	1154	1169	1174	1172
ν_{10}	A_g	1189	1205	1207	1162	1177	1177	1183
ν_{11}	B_{3u}	1722	1717	1652	1553	1545	1541	1603
ν_{12}	B_{2g}	1894	1860	1814	1745	1702	1699	1760
ν_{13}	B_{1u}	2039	1996	1984	1973	1835	1943	1925
ν_{14}	A_g	2192	2180	2153	2108	2111	2115	2088
ν_{15}	B_{3u}	2604	2609	2611	2509	2512	2516	2520
ν_{16}	A_g	2618	2621	2622	2520	2523	2526	2530
ν_{17}	B_{1g}	2695	2695	2690	2583	2580	2579	2596
ν_{18}	B_{2u}	2710	2710	2704	2594	2598	2598	2609
RMS		73.13	65.18	53.23	29.96	31.44	27.19	

^aRef. 68

the value of 22.8 cm^{-1} obtained with the CCSD(T) benchmark calculations. Thus, B3LYP-D2/cc-pVTZ was chosen for all other compounds.

3.2. $B_3H_8^-$

$B_3H_8^-$ has been reported as an intermediate during the decomposition of $Mg(BH_4)_2$ and $Y(BH_4)_3$ [7, 31, 69]. Olson and Boldyrev [70] have shown that this ion exists in different forms which can transform into each other by hydrogen migration. This fluxional behavior is seen experimentally by solution NMR studies [31, 71, 72]. Figure 2 shows two different conformations of $B_3H_8^-$.

The most stable one has two B-H-B bridges in C_{2v} symmetry (Figure 2a). Three equivalent isomers can be formed, and they transform into each other through the transition state of C_s symmetry shown in Figure 2. As with B_2H_6 , a series of calculations with different basis sets were performed both in the harmonic and anharmonic approach, including dis-

Table 4: RMS errors with respect to experimental data (in cm^{-1}) for the different levels of theory used to calculate the vibrational frequencies of B_2H_6

	Method	RMS error	RMS* error
Harmonic	MP2/6-31G*	133.82	114.70
	MP2/6-311++G**	94.34	80.33
Anharmonic	B3LYP/6-311++G**	59.15	52.94
	HF/cc-pVTZ	66.20	71.89
	M06-HF/cc-pVTZ	58.35	22.37
	PBE0/6-311++G**	32.86	30.67
	PBE0/cc-pVTZ	29.96	27.24
	PBE0/def2TZVP	29.74	27.11
	B3LYP/6-311++G**	37.67	18.87
	B3LYP/cc-pVTZ	31.44	14.05
	B3LYP/def2TZVP	31.13	15.24
	CCSD(T)/cc-pVTZ	22.76	24.87
Adding Dispersion	B3LYP-D2/cc-pVTZ	27.19	19.01
	B3LYP-D3/cc-pVTZ	35.68	17.18
	B3LYP-D3BJ/cc-pVTZ	32.39	14.98

*The RMS error of vibrational frequencies excluding the $\text{B-H}_{\text{bridge}}$ modes

persion corrections. Comparison with the experimental vibrational frequencies showed that the smallest RMS is obtained using B3LYP-D2/cc-pVTZ, as previously found for B_2H_6 . As expected, the structural parameters do not change very much with the different levels of calculations (see Supplorting Information). These parameters agree with the reported experimental values. Note that in contrast to B_2H_6 , the B-H-B bridges are not symmetrical, with B-H bond distances of 1.49 and 1.26 Å respectively. Olson and Boldyrev [70] obtained a zero-point energy difference of 1.2 kcal/mol (5.0 kJ/mol) between the ground state and the transition state using B3LYP/6-311++ G**. We obtain 1.1 kcal/mol (4.6 kJ/mol). An imaginary frequency of $151i \text{ cm}^{-1}$ is obtained for the first-order transition state.

3.2.1. NMR chemical shifts of B_3H_8^-

The NMR chemical shifts are summarized in Table 5. Experimentally, only one peak is seen both in the ^{11}B and ^1H NMR spectra, confirming the fluxional behavior of this ion [12, 31, 70–72]. For ^{11}B , the experimental value is -30.8 or -30.4 ppm, which is close to the average of the calculated static values indicated in Table 5. Similarly, the average value for the chemical shift of ^1H is close to the experimental value of 0.2 ppm.

Figure 2: Two possible structures of $B_3H_8^-$: (a) at its lowest-energy minimum with C_{2v} symmetry, and (b) at its transition state of C_s symmetry (B3LYP-D2/cc-pVTZ results).

Table 5: Calculated ^{11}B and 1H NMR chemical shifts of $B_3H_8^-$ (in ppm) relative to $BF_3 \cdot OEt_2$ and TMS, respectively

	$\delta^{11}B$			δ^1H			
	(1B)	(2B)	Average	(2H)	(4H)	(2H)	Average
B3LYP/6-311++G**	-11.9	-48.8	-36.5	-1.03	-0.02	2.21	0.29
B3LYP/cc-pVTZ	-14.9	-51.8	-39.5	-1.16	-0.14	2.05	0.15
B3LYP-D2/cc-pVTZ	-14.3	-51.4	-39.0	-1.13	-0.12	2.06	0.17
Exp.			-30.8, ^a -30.4 ^b				0.2 ^a

^aRef. 73, ^bRefs. 6, 74

3.2.2. Vibrational spectroscopy of $B_3H_8^-$

$B_3H_8^-$ has 27 vibrational modes. The normal modes of B_3H_8 transform as $9A_1$, $5A_2$, $6B_1$, and $7B_2$. The A_1 , B_1 , and B_2 modes are both IR and Raman active, while the A_2 mode is only Raman active. The calculated and experimental frequencies [75, 76] are compared in Table 6. Note that the experimental frequencies are somewhat scattered for different samples (NaB_3H_8 , CsB_3H_8) and experimental techniques (IR, Raman, INS). The 8 highest frequencies correspond to B-H stretching modes which are observed between 2080 and 2479 cm^{-1} . Using B3LYP-D2/cc-pVTZ, the corresponding harmonic frequencies stretch from 2187 to 2518 cm^{-1} , while the anharmonic frequencies range from 2058 to 2399 cm^{-1} .

As for B_2H_6 , the RMS decreases when anharmonicity and dispersion correction are in-

Table 6: Calculated B3LYP-D2/cc-pVTZ harmonic and anharmonic frequencies of B_3H_8^- , and RMS errors with respect to experimental IR data (in cm^{-1})

Mode	Symm	Calculated		Exp.*		
		Har	Anhar	IR ^a	Raman ^b	INS ^c
ν_1	A_2	205	179			
ν_2	B_1	433	408			
ν_3	B_2	494	392	462		472
ν_4	A_1	524	488		555	580
ν_5	A_1	721	658			
ν_6	B_1	735	706			
ν_7	B_2	805	749	791	792	
ν_8	A_2	837	794			
ν_9	A_1	835	828			
ν_{10}	B_1	918	870			
ν_{11}	A_2	1017	968			
ν_{12}	B_2	1068	1021	1013		
ν_{13}	B_1	1093	1046		1050	
ν_{14}	A_2	1186	1078		1116	
ν_{15}	A_1	1196	1142	1178	1185	
ν_{16}	B_2	1202	1143			
ν_{17}	A_1	1218	1168			
ν_{18}	B_2	1299	1134		1218	
ν_{19}	A_1	1414	1303			
ν_{20}	B_2	2187	2058	2092	2088	
ν_{21}	A_1	2229	2131	2130	2132	
ν_{22}	B_2	2468	2367	2338	2330	
ν_{23}	A_1	2480	2373	2364	2370	
ν_{24}	A_1	2483	2387			
ν_{25}	A_2	2493	2376			
ν_{26}	B_1	2505	2375	2432		
ν_{27}	B_1	2518	2399	2479	2455	
RMS		79	43			

*Refs. 75 and 75. ^aThe Infrared spectra of CsB_3H_8 in solution, ^bThe Raman spectra of solid CsB_3H_8 [76], ^cThe Neutron scattering spectra of solid CsB_3H_8 at 77 K [75].

cluded in the calculations (Table 7), however the value of 43 cm^{-1} is still quite large. Inspection of Table 6 shows that the modes ν_3 and ν_{18} , which correspond to the motions of the bridging hydrogens, contribute largely to the RMS. Thus, at the B3LYP-D2/cc-pVTZ level, for mode ν_3 , the calculated anharmonic frequency is 392 cm^{-1} and the observed one is 455-

Table 7: RMS errors of calculated harmonic and anharmonic frequencies of $B_3H_8^-$ (in cm^{-1})

	B3LYP		B3LYP/cc-pVTZ				
	6-311++G**		Without D		D2	D3	D3BJ
	Har.	Anhar.	Har	Anhar.	Anhar.		
	RMS						
	52	66	63	57	43	64	59

Har.: harmonic; Anhar.: Anharmonic

472 cm^{-1} ; and for mode ν_{18} , the predicted calculated anharmonic frequency is 1134 cm^{-1} while the observed one is $1218\text{-}1255\text{ cm}^{-1}$. Combining the results for B_2H_6 and $B_3H_8^-$, it appears that the B- H_{bridge} stretching and bending frequencies are subject to the largest discrepancies between experimental and theoretical values and call for caution when comparing experimental and theoretical spectra. However, the lower frequency spectral region (below 1000 cm^{-1}) appears to be satisfactorily described in the anharmonic approximation.

In total, we have studied the following 21 boron-hydrogen species: BH_3 , BH_4^- , B_2H_6 , $B_2H_7^-$, $B_3H_8^-$, B_4H_{10} , $B_4H_9^-$, $B_5H_5^{2-}$, B_5H_9 , B_5H_{11} , $B_6H_6^{2-}$, B_6H_{10} , B_6H_{12} , $B_7H_7^{2-}$, $B_8H_8^{2-}$, B_8H_{12} , $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{10}H_{14}$, $B_{11}H_{11}^{2-}$, $B_{12}H_{12}^{2-}$. The results for each individual species are summarized in the supplementary material together with corresponding literature data. In the following sections, we summarize the general trends resulting from these calculations.

3.3. General trends in the vibrational and in the NMR spectroscopic data

3.3.1. NMR ^{11}B chemical shifts

Figure 3 shows that there is a good correlation between experimental (δ_{exp}) and calculated (δ_{calc}) values of the ^{11}B chemical shift. The experimental values were retrieved from the literature [11, 12, 17, 60, 72, 77, 78] and from the on-line database of the Cole research group [79]. Using B3LYP-D2/cc-pVTZ, the fitting equation is: $\delta_{\text{exp}} = 0.921 \delta_{\text{calc}} + 4.082\text{ ppm}$ with $R^2 = 0.993$. This shows that in this case, the calculated values of the chemical shift are systematically smaller than the experimental values and that one has systematic errors of several ppm. Using B3LYP/6311++G**, the fitting equation becomes $\delta_{\text{exp}} = 0.926 \delta_{\text{calc}} + 1.830\text{ ppm}$ (see Supporting Information), which is in closer agreement with experiment.

3.3.2. Vibrational frequencies

Figure 4 compares the calculated anharmonic frequencies with the corresponding experimental data for 11 compounds in the low frequency region (below 1500 cm^{-1}). The

Figure 3: Correlation between calculated and experimental ^{11}B chemical shifts (B3LYP-D2/cc-pVTZ results).

correlation is very good with a slope very close to 1 (0.996). This correlation shows that in this spectral region, the calculated values are typically and systematically $14(\pm 8) \text{ cm}^{-1}$ smaller than the experimental values. This is illustrated in the Raman spectrum of $\text{B}_{10}\text{H}_{14}$ shown below.

In the case of B_2H_7^- for which the bent or linear nature of its B-H-B bridge has long been debated, the calculations were performed using the accepted bent model of C_2 symmetry [9, 80–84]. The very good agreement observed in Figure 4 between experimental and calculated anharmonic frequencies support the C_2 model. However, an imaginary anharmonic frequency is obtained for the vibrational mode of lowest harmonic frequency (see Supporting Information). For such a soft mode, which is associated to the motion of the bridging H atom along the C_2 axis, this actually indicates a breakdown of the validity of the anharmonic treatment that follows from the fact that the potential energy surface (PES) is flat around the two possible C_2 minima (the PES along this mode can indeed be viewed as a double-well potential with a small to vanishing barrier).

Figure 4: Correlation between the calculated anharmonic and the experimental vibrational frequencies for the low frequency region (B3LYP-D2/cc-pVTZ results).

Figure 5: Comparison of the calculated harmonic and anharmonic Raman spectra with the experimental Raman spectrum (532 nm, room temperature) of solid $B_{10}H_{14}$ below 1500 cm^{-1} (B3LYP-D2/cc-pVTZ results).

Figure 5 compares the calculated harmonic and anharmonic Raman spectra with the experimental Raman spectrum of $B_{10}H_{14}$ below 1500 cm^{-1} . This Figure clearly highlights the improvement of the agreement achieved using the anharmonic calculations. Below 800 cm^{-1} , the harmonic calculation reproduces very well the experimental data. However, the bands calculated above 1050 cm^{-1} are far away from the experimental results. With the anharmonic calculation, one obtains a much better agreement above 800 cm^{-1} , but in the region between 500 and 700 cm^{-1} several weak bands do not match well with the experimental data.

The overall agreement in the B-H stretching mode region (above 2000 cm^{-1}) is not so good. In the graph of the experimental frequencies (ν_{exp}) *vs* calculated anharmonic frequencies ($\nu_{\text{calc}}^{\text{anh}}$; Figure 6), the data are somewhat scattered and yield a fitting equation $\nu_{\text{exp}} = 0.937\nu_{\text{calc}}^{\text{anh}} + 175.9$ with a rather poor $R^2 = 0.898$. The scatter of the data can be explained in part by the fact that at this stage, we did not consider the strong Fermi resonances which can occur, as we previously quantitatively did for BH_4^- [85]. If one plots the calculated harmonic frequencies ($\nu_{\text{calc}}^{\text{harm}}$) *versus* the anharmonic frequencies between

Figure 6: Correlation between the calculated anharmonic and the experimental vibrational frequencies for the high frequency region (B3LYP-D2/cc-pVTZ results).

2000 and 2650 cm^{-1} , one obtains an excellent correlation ($R^2 = 0.994$) with the equation $\nu_{\text{calc}}^{\text{anh}} = \nu_{\text{calc}}^{\text{harm}} - 119.6$, *i.e.* the harmonic frequencies are systematically *ca.* 120 cm^{-1} larger than the experimental ones. Globally, it appears that the harmonic B-H stretching frequencies are closer to the experimental values, while the anharmonic calculations somewhat underestimate these frequencies.

4. Conclusion

Using B3LYP-D2/cc-pVTZ, we have systematically studied 21 boron-hydrogen species. We have calculated harmonic and anharmonic vibrational frequencies as well as NMR chemical shifts. The comparison with available experimental vibrational data shows that the inclusion of anharmonicity significantly improves the agreement, especially below 1200 cm^{-1} . The motions of bridging hydrogen atoms being strongly anharmonic, the agreement between experiment and theory turns out to remain limited for these vibrations. Figure 5 illustrates both the advantages and limitations of the anharmonic calculations and suggests that, within the perturbational anharmonic framework of the calculations, one should use

both harmonic and anharmonic results for comparison with experimental data. The large anharmonic effects that could be evidenced also show that the inclusion of anharmonicity is key for the accurate prediction of the thermochemistry of these $B_xH_y^{z-}$ species (work in progress). Finally, the ^{11}B NMR spectra calculated with different approaches (in our case, B3LYP-D2/cc-pPVTZ and B3LYP/6311++G**) show excellent correlations with experimental data. We believe that these calculations as well as the methodology used will be helpful to identify intermediate decomposition products in the study of potential hydrogen storage materials.

In this paper, we have calculated the properties of $B_xH_y^{z-}$ species in the gas phase. In solids, their spectroscopic properties may change somewhat due the influence of their environment in crystals. Thus, in the case of BH_4^- , we have observed [86] that the IR active B-H stretching frequency can vary from 2210 cm^{-1} to 2380 cm^{-1} depending on the crystalline surroundings. The bending frequencies may additionally be influenced by the number of coordinating cations. Another aspect is the lowering of symmetry in the crystal, which can lead to significant splitting and additional bands due to the modified selection rules. Using the GF method [86], it is in principle possible to predict the extent of these splittings. Alternatively, one can theoretically simulate this lower symmetry, as was shown with DFT calculations on a $\text{Li}_2\text{B}_{12}\text{H}_{12}$ cluster in the gas phase [87]. B_3H_8^- can bind in both a bidentate or a tridentate way with its hydrogen atoms to metals [88]. In the complex $(\text{CO})_3\text{Mn}(\text{B}_3\text{H}_8)$ [89], there are 3 bridging B-H-Mn bonds, and the bridging B-H-B bonds are maintained. In this case, one should calculate the vibrational properties of the entire complex, as was also reported previously for complex borohydride ions such as $\text{Sc}(\text{BH}_4)_4^-$ [90] and for those present in the $\text{AZn}_2(\text{BH}_4)_5$ ($\text{A} = \text{Li}, \text{Na}$) and $\text{NaZn}(\text{BH}_4)_3$ compounds [91]. In the case of the compounds with BH_4^- , the librational frequencies can reach frequencies of about 500 cm^{-1} . However, with increasing size of the BH_4^- ions, these frequencies will tend towards lower energies and thus the librational modes interact less with internal modes of the ions. In the case of $\text{Na}_2\text{B}_{12}\text{H}_{12}$, a periodic DFT calculation has been performed [92]: the calculated translational and librational modes range up to 175 cm^{-1} , while the lowest frequency internal mode appears at 532 cm^{-1} . The reactivity of species with bridging

hydrogen bonds cannot be simply predicted by the results obtained in this paper, as it can be assumed that the presence of a metal ion next to the $B_xH_y^{z-}$ ions will significantly modify the electron densities of the borohydrides. This topic will be addressed in the future to gain more information about possible decomposition reactions pathways of borohydrides for hydrogen storage.

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Supporting Information

The Supporting Information consists of two files. The supporting material referred to in the text is given in the first file. The second file collects calculated and available experimental vibrational and NMR data for all the studied species.

- [1] F. Schlüter, E. Bernhardt, Syntheses and Crystal Structures of the closo-Borates $M_2[B_7h_7]$ and $M[B_7h_8]$ ($M = PPh_4$, PNP, and $N(n-Bu_4)$): the Missing Crystal Structure in the Series $[b_nh_n]^{2-}$ ($n = 6-12$), *Inorg. Chem.* 50 (6) (2011) 2580–2589. doi:10.1021/ic102434t.
URL <http://dx.doi.org/10.1021/ic102434t>
- [2] A. V. Kopytin, K. Y. Zhizhin, Y. I. Urusov, V. N. Mustyatsa, Y. V. Kokunov, N. T. Kuznetsov, Ion-selective electrodes for the determination of closoborate anions, *J. Anal. Chem.* 66 (7) (2011) 666–669. doi:10.1134/S1061934811070070.
URL <http://link.springer.com/article/10.1134/S1061934811070070>
- [3] A. Y. Bykov, G. A. Razgonyaeva, N. N. Mal'tseva, K. Y. Zhizhin, N. T. Kuznetsov, A new method of synthesis of the $B_3h_8^-$ anion, *Russ. J. Inorg. Chem.* 57 (4) (2012) 471–473. doi:10.1134/S0036023612040055.
URL <http://link.springer.com/article/10.1134/S0036023612040055>
- [4] A. Y. Bykov, N. N. Mal'tseva, N. B. Generalova, K. Y. Zhizhin, N. T. Kuznetsov, Reactions of sodium tetrahydroborate with alkyl and aryl halides: A new approach to the synthesis of $B_3h_8^-$ and $b_{12}h_{12}^{2-}$ anions, *Russ. J. Inorg. Chem.* 58 (11) (2013) 1321–1323. doi:10.1134/S003602361311003X.
URL <http://link.springer.com/article/10.1134/S003602361311003X>
- [5] A. Y. Bykov, K. Y. Zhizhin, N. T. Kuznetsov, The chemistry of the octahydrotriborate anion $B_3h_8^-$, *Russ. J. Inorg. Chem.* 59 (13) (2014) 1539–1555. doi:10.1134/S0036023614130026.
URL <http://link.springer.com/article/10.1134/S0036023614130026>
- [6] Z. Huang, H. K. Lingam, X. Chen, S. Porter, A. Du, P. M. Woodard, S. G. Shore, J.-C. Zhao, Synthesis, structural analysis, and thermal decomposition studies of $[(NH_3)_2bh_2]B_3h_8$, *RSC Adv.* 3 (20) (2013) 7460–7465, 00000. doi:10.1039/C3RA22836C.
URL <http://pubs.rsc.org/en/content/articlelanding/2013/ra/c3ra22836c>
- [7] Y. Yan, A. Remhof, D. Rentsch, Y.-S. Lee, Y. W. Cho, A. Züttel, Is $Y_2(B_{12}H_{12})_3$ the main intermediate in the decomposition process of $Y(BH_4)_3$?, *Chem. Commun.* 49 (45) (2013) 5234–5236.
- [8] R. A. Beaudet, In *Advances in Boron and Boranes*, VCH, 1988, Ch. 20, p. 417.
- [9] M. Bühl, P. v. R. Schléyer, Application and evaluation of ab initio chemical shift calculations for boranes and carboranes. how reliable are "accurate" experimental structures?, *J. Am. Chem. Soc.* 114 (1992) 477–491.

- [10] M. Bühl, J. Gauss, M. Hofmann, P. v. R. Schléyer, Decisive electron correlation effects on computed boron-11 and carbon-13 nmr chemical shifts. application of the *giao*-mp2 method to boranes and carboranes, *J. Am. Chem. Soc.* 115 (26) (1993) 12385–12390. doi:10.1021/ja00079a020.
- [11] Z. Łodziana, P. Błonski, Y. Yan, D. Rentsch, A. Remhof, Nmr chemical shifts of ^{11}B in metal borohydrides from first-principle calculations, *J. Phys. Chem. C* 118 (13) (2014) 6594–6603. doi:10.1021/jp4120833.
- [12] M. L. McKee, W. N. Lipscomb, Ab initio study of the transient boron hydrides B_3H_7 , B_3H_9 , B_4H_8 , and B_4H_{12} and the fluxional anion B_3H_8^- , *Inorg. Chem.* 21 (7) (1982) 2846–2850. doi:10.1021/ic00137a060.
- [13] M. L. McKee, Z.-X. Wang, P. v. R. Schléyer, Ab Initio Study of the Hypercloso Boron Hydrides B_nH_n and B_nH_n^- . Exceptional Stability of Neutral $\text{B}_{13}\text{H}_{13}$, *J. Am. Chem. Soc.* 122 (19) (2000) 4781–4793, 00000. doi:10.1021/ja994490a.
URL <http://dx.doi.org/10.1021/ja994490a>
- [14] P. Meier, M. Neff, G. Rauhut, Accurate vibrational frequencies of borane and its isotopologues, *J. Chem. Theory Comput.* 7 (1) (2011) 148–152. doi:10.1021/ct1004752.
- [15] M. T. Nguyen, M. H. Matus, D. A. Dixon, Heats of Formation of Boron Hydride Anions and Dianions and Their Ammonium Salts $[\text{B}_n\text{H}_m^y][\text{NH}_4^+]_y$ with $y = 1-2$, *Inorg. Chem.* 46 (18) (2007) 7561–7570, 00000. doi:10.1021/ic700941c.
URL <http://dx.doi.org/10.1021/ic700941c>
- [16] A. P. Scott, L. Radom, Harmonic vibrational frequencies: An evaluation of hartree-fock, møller-plesset, quadratic configuration interaction, density functional theory, and semiempirical scale factors, *J. Phys. Chem.* 100 (41) (1996) 16502–16513. doi:10.1021/jp960976r.
- [17] L. J. Todd, A. R. Siedle, Nmr studies of boranes, carboranes and hetero-atom boranes, *Progress in NMR Spectroscopy* 13 (1979) 87–176.
- [18] A. X. Tian, Ab initio and electron propagator theory study of boron hydrides, *J. Phys. Chem. A* 109 (2005) 5471–5480.
- [19] D. A. Wann, P. D. Lane, H. E. Robertson, J. Holub, D. Hnyk, Structures of, and related consequences of deprotonation on, two c_s -symmetric *arachno* nine-vertex heteroboranes, 4,6- $\text{x}_2\text{b}_7\text{h}_9$ ($\text{x} = \text{ch}_2$; s) studied by gas electron diffraction/quantum chemical calculations and *giao*/nmr, *Inorg. Chem.* 52 (8) (2013) 4502–4508, pMID: 23541164. arXiv:<http://dx.doi.org/10.1021/ic302776d>, doi:10.1021/ic302776d.
URL <http://dx.doi.org/10.1021/ic302776d>
- [20] S. Muhammad, H. Xu, Y. Liao, Y. Kan, Z. Su, Quantum mechanical design and structure of the li@b10h14 basket with a remarkably enhanced electro-optical response, *J. Am. Chem. Soc.* 131 (33) (2009) 11833–11840, pMID: 19642644. arXiv:<http://dx.doi.org/10.1021/ja9032023>, doi:10.1021/ja9032023.
URL <http://dx.doi.org/10.1021/ja9032023>
- [21] S. Muhammad, H. Xu, Z. Su, Capturing a synergistic effect of a conical push and an inward pull in fluoro derivatives of li@b10h14 basket: Toward a higher vertical ionization potential and nonlinear optical response, *J. Phys. Chem. A* 115 (5) (2011) 923–931, pMID: 21226521. arXiv:<http://dx.doi.org/10.1021/jp110401f>, doi:10.1021/jp110401f.
URL <http://dx.doi.org/10.1021/jp110401f>
- [22] M. Garcia-Borràs, M. Solà, J. M. Luis, B. Kirtman, Electronic and vibrational nonlinear optical properties of five representative electrides, *J. Chem. Theory Comput.* 8 (8) (2012) 2688–2697. arXiv:<http://dx.doi.org/10.1021/ct300433q>, doi:10.1021/ct300433q.
URL <http://dx.doi.org/10.1021/ct300433q>
- [23] L. Schlappbach, A. Züttel, Hydrogen-storage materials for mobile applications, *Nature* 414 (6861) (2001) 353–358. doi:10.1038/35104634.
URL <http://dx.doi.org/10.1038/35104634>
- [24] A. Züttel, A. Borgschulte, S.-I. Orimo, Tetrahydroborates as new hydrogen storage materials, *Scr. Mater.* 56 (10) (2007) 823–828. doi:10.1016/j.scriptamat.2007.01.010.

- [25] S.-I. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, C. M. Jensen, Complex hydrides for hydrogen storage, *Chem. Rev.* 107 (10) (2007) 4111–4132. doi:10.1021/cr0501846.
- [26] M. Fichtner, K. Chlopek, M. Longhini, H. Hagemann, Vibrational spectra of $\text{Ca}(\text{BH}_4)_2$, *J. Phys. Chem. C* 112 (30) (2008) 11575–11579. doi:10.1021/jp801482b.
URL <http://dx.doi.org/10.1021/jp801482b>
- [27] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S.-I. Towata, A. Züttel, S.-I. Orimo, Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativities: First-principles calculations and experiments, *Phys. Rev. B* 74 (4) (2006) 045126. doi:10.1103/PhysRevB.74.045126.
- [28] J.-H. Kim, J.-H. Shim, Y. W. Cho, On the reversibility of hydrogen storage in ti- and nb-catalyzed $\text{Ca}(\text{BH}_4)_2$, *J. Power Sources* 181 (1) (2008) 140–143. doi:10.1016/j.jpowsour.2008.02.094.
- [29] Y. Liu, S. Giri, J. Zhou, P. Jena, Intermediate phases during decomposition of metal borohydrides, $\text{M}(\text{BH}_4)_n$ ($m=\text{na, mg, y}$), *J. Phys. Chem. C* 118 (2014) 28456. doi:10.1021/jp509223d.
- [30] M. Paskevicius, M. P. Pitt, C. J. Webb, D. A. Sheppard, U. Filsø, E. M. Gray, C. E. Buckley, In-situ x-ray diffraction study of $\gamma\text{-Mg}(\text{BH}_4)_2$ decomposition, *J. Phys. Chem. C* 116 (29) (2012) 15231–15240. doi:10.1021/jp302898k.
- [31] M. Chong, A. Karkamkar, T. Autrey, S.-I. Orimo, S. Jalisatgi, C. M. Jensen, Reversible dehydrogenation of magnesium borohydride to magnesium triborane in the solid state under moderate conditions, *Chem. Commun.* 47 (4) (2011) 1330–1332, 00033. doi:10.1039/C0CC03461D.
- [32] R. J. Newhouse, V. Stavila, S.-J. Hwang, L. E. Klebanoff, J. Z. Zhang, Reversibility and improved hydrogen release of magnesium borohydride, *J. Phys. Chem. C* 114 (11) (2010) 5224–5232. doi:10.1021/jp9116744.
- [33] H.-W. Li, K. Miwa, N. Ohba, T. Fujita, T. Sato, Y. Yan, S. Towata, M. W. Chen, S. Orimo, Formation of an intermediate compound with a $\text{B}_{12}\text{H}_{12}$ cluster: experimental and theoretical studies on magnesium borohydride $\text{Mg}(\text{BH}_4)_2$, *Nanotechnology* 20 (20) (2009) 204013. doi:10.1088/0957-4484/20/20/204013.
- [34] S.-J. Hwang, R. C. Bowman, J. W. Reiter, J. W. Rijssenbeek, G. L. Soloveichik, J.-C. Zhao, H. Kabbour, C. C. Ahn, NMR confirmation for formation of $[\text{B}_{12}\text{H}_{12}]^{2-}$ complexes during hydrogen desorption from metal borohydrides, *J. Phys. Chem. C* 112 (9) (2008) 3164–3169. doi:10.1021/jp710894t.
- [35] N. Ohba, K. Miwa, M. Aoki, T. Noritake, S.-I. Towata, Y. Nakamori, S.-I. Orimo, A. Züttel, First-principles study on the stability of intermediate compounds of LiBH_4 , *Phys. Rev. B* 74 (7) (2006) 075110, 00000. doi:10.1103/PhysRevB.74.075110.
- [36] M. Sharma, D. Sethio, V. D’Anna, H. Hagemann, Theoretical study of species, *Int. J. Hydrogen Energ.* 40 (37) (2015) 12721–12726. doi:http://dx.doi.org/10.1016/j.ijhydene.2015.07.125.
URL <http://www.sciencedirect.com/science/article/pii/S036031991501928X>
- [37] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* 136 (1964) B864–B871.
- [38] W. Kohn, L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (1965) A1133–A1138.
- [39] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Å. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09 Revision D.01, gaussian Inc. Wallingford CT 2009.
- [40] Gaussian NEWS, v. 5, no. 2, summer 1994, p. 2. “Becke3LYP Method References and General Citation Guidelines”.

- [41] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* 98 (7) (1993) 5648–5652. doi:doi:10.1063/1.464913.
URL http://jcp.aip.org/resource/1/jcpsa6/v98/i7/p5648_s1
- [42] J. P. Perdew, M. Ernzerhof, K. Burke, Rationale for mixing exact exchange with density functional approximations, *J. Chem. Phys.* 105 (1996) 9982–9985.
- [43] C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: The pbe0 model, *J. Chem. Phys.* 110 (1999) 6158–6170.
- [44] Y. Zhao, D. G. Truhlar, Density functional for spectroscopy: No long-range self-interaction error, good performance for rydberg and charge-transfer states, and better performance on average than b3lyp for ground states, *J. Phys. Chem. A* 110 (2006) 13126–13130.
- [45] S. Grimme, Semiempirical gga-type density functional constructed with a long-range dispersion correction, *J. Comput. Chem.* 27 (2006) 1787–1799.
- [46] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements h-pu, *J. Chem. Phys.* 132 (2010) 154104.
- [47] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.* 21 (2011) 1456–1465.
- [48] C. Møller, M. S. Plesset, Note on an approximation treatment for many-electron systems, *Phys. Rev.* 46 (1934) 618–622. doi:10.1103/PhysRev.46.618.
URL <http://link.aps.org/doi/10.1103/PhysRev.46.618>
- [49] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, A fifth-order perturbation comparison of electron correlation theories, *Chem. Phys. Lett.* 157 (1989) 479–483.
- [50] P. C. Hariharan, J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theoret. Chimica Acta* 28 (1973) 213–222.
- [51] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. Pople, Self-consistent molecular orbital methods. xxiii. a polarization-type basis set for second-row elements, *J. Chem. Phys.* 77 (1982) 3654–3665.
- [52] K. Raghavachari, J. S. Binkley, R. Seeger, J. A. Pople, Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions, *J. Chem. Phys.* 72 (1980) 650–654.
- [53] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, Efficient diffuse function-augmented basis sets for anion calculations. iii. the 3-21+g basis set for first-row elements, li–f, *J. Comput. Chem.* 4 (3) (1983) 294–301. doi:10.1002/jcc.540040303.
URL <http://dx.doi.org/10.1002/jcc.540040303>
- [54] F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* 7 (2005) 3297–3305.
- [55] T. H. Dunning, Jr., Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen, *J. Chem. Phys.* 90 (1989) 1007–1023.
- [56] V. Barone, Vibrational zero-point energies and thermodynamic functions beyond the harmonic approximation, *J. Chem. Phys.* 120 (7) (2004) 3059–3065. doi:<http://dx.doi.org/10.1063/1.1637580>.
- [57] V. Barone, Anharmonic vibrational properties by a fully automated second-order perturbative approach, *J. Chem. Phys.* 122 (1) (2005) 014108. doi:10.1063/1.1824881.
- [58] J. Bloino, V. Barone, A second-order perturbation theory route to vibrational averages and transition properties of molecules: General formulation and application to infrared and vibrational circular dichroism spectroscopies, *J. Chem. Phys.* 136 (12) (2012) 124108. doi:10.1063/1.3695210.
- [59] J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, A comparison of models for calculating nuclear magnetic resonance shielding tensors, *J. Chem. Phys.* 104 (14) (1996) 5497–5509. doi:10.1063/1.471789.
URL <http://scitation.aip.org/content/aip/journal/jcp/104/14/10.1063/1.471789>
- [60] S. Heřmánek, {NMR} as a tool for elucidation of structures and estimation of electron distribution in boranes and their derivatives, *Inorg. Chim. Acta* 289 (12) (1999) 20 – 44. doi:<http://dx.doi.org/>

- 10.1016/S0020-1693(99)00055-9.
 URL <http://www.sciencedirect.com/science/article/pii/S0020169399000559>
- [61] A. D. Norman, W. D. Jolly, *Inorg. Synth.* 11 (1968) 15.
- [62] W. N. Lipscomb, *Boron Hydrides*, W. A. Benjamin, New York, 1963.
- [63] A. Torabi, Y. Song, V. N. Staroverov, Pressure-induced polymorphic transitions in crystalline diborane deduced by comparison of simulated and experimental vibrational spectra, *J. Phys. Chem. C* 117 (5) (2013) 2210–2215. doi:10.1021/jp3100415.
- [64] D. Begue, C. Pouchan, J.-C. Guillemin, A. Benidar, Anharmonic treatment of vibrational resonance polyads - the diborane: a critical case for numerical methods, *Theor. Chem. Acc.* 131 (3) (2012) 1122. doi:10.1007/s00214-012-1122-1.
- [65] J. Duncan, J. Harper, The structure of the diborane molecule, *Mol. Phys.* 51 (2) (1984) 371–380, 00043. doi:10.1080/00268978400100251.
- [66] L. S. Bartell, B. L. Carrol, *J. Chem. Phys.* 42 (-) (1965) 1135. doi:-.
- [67] T. P. Onak, H. L. Landersman, R. E. Williams, I. Shapiro, *J. Chem. Phys.* (1959) 533.
- [68] J. L. Duncan, J. Harper, E. Hamilton, G. D. Nivellini, The empirical harmonic potential function of diborane, *J. Mol. Spectrosc.* 102 (2) (1983) 416–440, 00032. doi:10.1016/0022-2852(83)90052-8.
- [69] M. Chong, M. Matsuo, S.-I. Orimo, T. Autrey, C. M. Jensen, Selective Reversible Hydrogenation of $\text{mg}(\text{b}_3\text{h}_8)_2/\text{mg}\text{h}_2$ to $\text{Mg}(\text{BH}_4)_2$: Pathway to Reversible Borane-Based Hydrogen Storage?, *Inorg. Chem.* 54 (8) (2015) 4120–4125. doi:10.1021/acs.inorgchem.5b00373.
 URL <http://dx.doi.org/10.1021/acs.inorgchem.5b00373>
- [70] J. K. Olson, A. I. Boldyrev, Ab initio characterization of the flexural anion found in the reversible dehydrogenation, *Comput. Theor. Chem.* 967 (1) (2011) 1–4. doi:10.1016/j.comptc.2011.04.011.
- [71] C. H. Bushweller, H. Beall, M. Grace, W. J. Dewkett, H. S. Bilofsky, Temperature dependence of the proton nuclear magnetic resonance spectra of copper(i) borane complexes, b_3h_8^- salts, and icosahedral carboranes. quadrupole-induced spin decoupling. fluxional behavior, *J. Am. Chem. Soc.* 93 (9) (1971) 2145–2149. doi:10.1021/ja00738a009.
- [72] H. Beall, C. H. Bushweller, W. J. Dewkett, M. Grace, Intramolecular exchange and "thermal" decoupling in B_3H_8 -compounds, *J. Am. Chem. Soc.* 92 (11) (1970) 3484–3486. doi:10.1021/ja00714a053.
- [73] Y. Yan, A. Remhof, P. Mauron, D. Rentsch, Z. Lodziana, Y.-S. Lee, H.-S. Lee, Y. W. Cho, A. Züttel, Controlling the dehydrogenation reaction toward reversibility of the LiBH_4 - $\text{Ca}(\text{BH}_4)_2$ eutectic system, *J. Phys. Chem. C* 117 (17) (2013) 8878–8886. doi:10.1021/jp401628g.
- [74] Z. Huang, X. Chen, T. Yisgedu, J.-C. Zhao, S. G. Shore, High-capacity hydrogen release through hydrolysis of NaB_3H_8 , *Int. J. Hydrogen Energ.* 36 (12) (2011) 7038–7042. doi:10.1016/j.ijhydene.2011.03.033.
 URL <http://www.sciencedirect.com/science/article/pii/S0360319911006227>
- [75] J. Tomkinson, C. J. Ludman, T. C. Waddington, The i.r., raman and inelastic neutron scattering spectra of caesium octahydridotriborate, CsB_3H_8 , *Spectrochim. Acta Part A: Mol. Spectrosc.* 35 (2) (1979) 117–122. doi:10.1016/0584-8539(79)80171-3.
 URL <http://www.sciencedirect.com/science/article/pii/0584853979801713>
- [76] E. A. Il'inchik, R. V. Gulyaev, D. A. Svintsitskii, K. G. Myakishev, V. V. Volkov, The ESCA analysis of the B_3H_8^- anion, *Russ. J. Gen. Chem.* 80 (8) (2010) 1550–1556, 00001. doi:10.1134/S1070363210080025.
 URL <http://link.springer.com/article/10.1134/S1070363210080025>
- [77] S. Heřmánek, Boron-11 NMR spectra of boranes, main-group heteroboranes, and substituted derivatives. Factors influencing chemical shifts of skeletal atoms, *Chem. Rev.* 92 (2) (1992) 325–362. doi:10.1021/cr00010a007.
 URL <http://dx.doi.org/10.1021/cr00010a007>
- [78] F. Teixidor, C. Vinas, R. W. Rudolph, Rules for predicting the boron-11 NMR spectra of closo-boranes and closo-heteroboranes, *Inorg. Chem.* 25 (19) (1986) 3339–3345, 00047. doi:10.1021/ic00239a005.
 URL <http://dx.doi.org/10.1021/ic00239a005>
- [79] <http://www.chemistry.sdsu.edu/research/BNMR> (last accessed: August 10, 2015).

- [80] Y. Matsui, R. C. Taylor, Vibrational spectra and structure of the heptahydrodiborate ion, $[b_2h_7]^-$ in glycol ethers, *Spectrochim. Acta A* 45 (2) (1989) 299–304. doi:[http://dx.doi.org/10.1016/0584-8539\(89\)80137-0](http://dx.doi.org/10.1016/0584-8539(89)80137-0).
URL <http://www.sciencedirect.com/science/article/pii/0584853989801370>
- [81] K. Raghavachari, P. von Rague Schleyer, G. W. Spitznagel, Theoretical structure of the $b_2h_7^-$ anion, *J. Am. Chem. Soc.* 105 (18) (1983) 5917–5918. arXiv:<http://dx.doi.org/10.1021/ja00356a035>, doi:10.1021/ja00356a035.
- [82] S. G. Shore, S. H. Lawrence, M. I. Watkins, R. Bau, Structure of the $[b_2h_7]^-$ anion, *J. Am. Chem. Soc.* 104 (26) (1982) 7669–7670. arXiv:<http://dx.doi.org/10.1021/ja00390a053>, doi:10.1021/ja00390a053.
- [83] S. I. Khan, M. Y. Chiang, R. Bau, T. F. Koetzle, S. G. Shore, S. H. Lawrence, A neutron diffraction study of $[n(pph_3)_2]^+[b_2h_7]^-$ at 80 K, *J. Chem. Soc., Dalton Trans.* (1986) 1753–1757. doi:10.1039/DT9860001753.
URL <http://dx.doi.org/10.1039/DT9860001753>
- [84] A. M. Sapse, L. Osorio, An ab initio study of the $b_2h_7^-$ anion, *Inorg. Chem.* 23 (5) (1984) 627–628. arXiv:<http://dx.doi.org/10.1021/ic00173a030>, doi:10.1021/ic00173a030.
- [85] P. Carbonnière, H. Hagemann, Fermi Resonances of Borohydrides in a Crystalline Environment of Alkali Metals, *J. Phys. Chem. A* 110 (32) (2006) 9927–9933. doi:10.1021/jp062091d.
URL <http://dx.doi.org/10.1021/jp062091d>
- [86] V. D’Anna, L. M. Lawson Daku, H. Hagemann, Quantitative spectra-structure relations for borohydrides, *J. Phys. Chem. C* 119 (2015) 21868–21874. arXiv:<http://dx.doi.org/10.1021/acs.jpcc.5b06045>, doi:10.1021/acs.jpcc.5b06045.
URL <http://dx.doi.org/10.1021/acs.jpcc.5b06045>
- [87] L. He, H.-W. Li, H. Nakajima, N. Tumanov, Y. Filinchuk, S.-J. Hwang, M. Sharma, H. Hagemann, E. Akiba, Synthesis of a bimetallic dodecaborate $LiNaB_{12}H_{12}$ with outstanding superionic conductivity, *Chem. Mater.* 27 (16) (2015) 5483–5486. doi:10.1021/acs.chemmater.5b01568.
- [88] C. Serrar, A. Es-sofi, A. Boutalib, A. Ouassas, A. Jarid, Synthesis, structural characterization, and theoretical calculations of a new copper(i)-octahydrotriborate complex, *Inorg. Chem.* 39 (10) (2000) 2224–2226. doi:10.1021/ic990909m.
- [89] S. J. Hildebrandt, D. F. Gaines, J. C. Calabrese, Low-temperature crystal and molecular structure of tricarbonyl[octahydrotriborato(1-)]manganese, $(CO)_3MnB_3H_8$, *Inorg. Chem.* 17 (4) (1978) 790–794. doi:10.1021/ic50182a002.
- [90] H. Hagemann, M. Longhini, J. W. Kaminski, T. A. Wesolowski, R. Černý, N. Penin, M. H. Sørby, B. C. Hauback, G. Severa, C. M. Jensen, $LiSc(BH_4)_4$: A novel salt of Li^+ and discrete $Sc(BH_4)_4^{4-}$ complex anions, *J. Phys. Chem. A* 112 (33) (2008) 7551–7555. doi:10.1021/jp803201q.
- [91] R. Černý, K. C. Kim, N. Penin, V. D’Anna, H. Hagemann, D. S. Sholl, $AZn_2(BH_4)_5$ ($a = Li, Na$) and $NaZn(BH_4)_3$: Structural studies, *J. Phys. Chem. C* 114 (44) (2010) 19127–19133. doi:10.1021/jp105957r.
- [92] R. Caputo, S. Garroni, D. Olid, F. Teixidor, S. Surinach, M. D. Baro, Can $Na_2[B_{12}H_{12}]$ be a decomposition product of $NaBH_4$?, *Phys. Chem. Chem. Phys.* 12 (2010) 15093–15100. doi:10.1039/C0CP00877J.
URL <http://dx.doi.org/10.1039/C0CP00877J>

Graphical Abstract

A very good correlation is observed between the (B3LYP-D2/cc-pVTZ)-calculated anharmonic and the experimental vibrational frequencies for a series of boron-hydrogen species. As illustrated here for $B_{12}H_{12}^{2-}$ whose parallel (red) and perpendicular (blue) polarized Raman spectra are shown, the evidenced correlation provides a reliable means of identifying intermediate decomposition products in the study of potential hydrogen storage.