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Synthesis and Characterization of $NaBD_3H$, A Potential Structural Probe for Hydrogen Storage Materials

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Specifically labeled $NaBD_3H$ has been synthesized and characterized using X-ray diffraction, NMR, and vibrational spectroscopy. The isotopic purity of the compound, as estimated from NMR spectra, was found to be about 85% with the compound $NaBD_2H_2$ as the second product. IR spectra confirm the relatively strong intensity of the single B−H stretching mode predicted from DFT calculations. Anharmonic DFT calculations show that for the BD_3H^- ion Fermi resonances with the single B−H stretching mode are very limited, making this mode a promising structural probe for complex borohydrides which can be prepared by metathetical reactions.

Introduction

In the search for new hydrogen storage materials, tetrahydroborate compounds, $M(BH_4)_n$, (with M = metal cation and n = valence of the cation) have gained considerable interest, mainly due to their high gravimetric content of H.[1] In the course of the search for new materials, reactions of alkali borohydrides with metal chlorides and/or hydrides using ball milling techniques can be performed, but the structural characterization of the resulting products may be difficult due to the presence of several mixed phases or the low crystallinity of the products. Moreover, promising compounds such as $Ca(BH_4)_2$ undergo several phase transitions with increasing temperature, and the structural characterization of all phases remains to be completed.[2−4] In particular, the accurate determination of boron hydrogen bond length in solids is experimentally difficult.

To have a new structurally sensitive probe for the hydrogen atoms in borohydrides, we decided to prepare and characterize specifically labeled $NaBD_3H$ as a starting material for other complex borohydrides. This approach was motivated by the study of alkanes with isotopically isolated C−H bonds[5] which revealed both theoretically and experimentally a linear correlation between C−H stretching frequency and bond length. Previously, we have been able to correlate the totally symmetrical B−D stretching mode of the alkali borohydrides with B−D bond length[6] obtained from neutron diffraction data. However, a similar correlation for the B−H stretching mode of the alkali borohydrides fails. This is due to the presence of strong Fermi resonances which are present for both B−D and B−H stretching modes as shown for $NaBH_4$ and $NaBD_4$ in Figure 1 (see also Figure S1, Supporting Information, which shows a low-temperature Raman spectrum of KBH_4 in the stretching mode region). It can be seen that for both $NaBH_4$ and $NaBD_4$, instead of the single IR active antisymmetrical B−H (D) stretching mode at approximately 2284 (1682) cm^{-1}, several bands are observed, but the overall shape is different for the hydride and deuteride. These Fermi resonances have been quantitatively analyzed using anharmonic DFT calculations.[7]

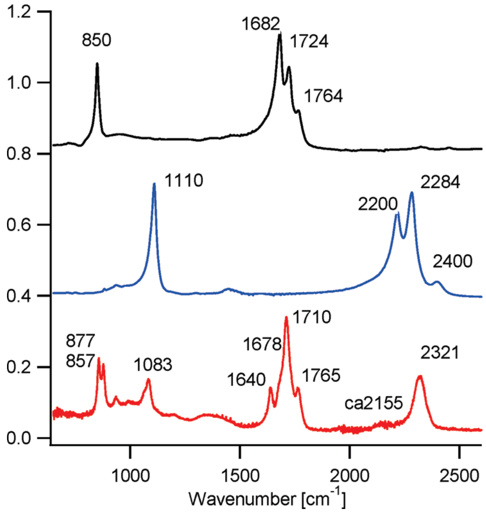

Figure 1. Room-temperature IR spectra of $NaBD_4$ (top), $NaBH_4$ (center), and $NaBD_3H$ (bottom). The spectra have been shifted vertically for clarity.

Further, experiments on slightly deuterated ammonium compounds (NH_4^+ is isoelectronic with BH_4^-) showed that in low symmetry crystals different orientations of the NH_3D^+ ion can be distinguished and subjected to infrared hole burning experiments.[8] Thus, a probe like BD_3H^- can give important and complementary information about the crystal structure, in particular about the local symmetry of the borohydride ion in the crystal.

To the best of our knowledge, there is only one pertinent report in the literature reporting on the selective synthesis of

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$NaBD_3H$ and $NaBH_3D$.[9] In this paper, we report on the preparation and characterization of $NaBD_3H$. Further, following our previous analysis of Fermi resonances in the alkali borohydrides using anharmonic DFT calculations,[7] we study theoretically the BD_3H^- ion with the same methodology to gain more insight into the potentially occurring Fermi resonances. Preliminary experimental results on $RbBD_3H$, obtained involuntarily as an impurity during a preparation of $RbBD_4$, are also included for comparison.

Experimental Section

All operations were carried out under an inert atmosphere using a Schlenk line or an argon-filled glovebox, where both the water and oxygen concentrations were kept below 1 ppm during operation.

Synthesis of the isotopic borohydride ion was performed by a direct wet chemical method based on a proposal made by Köster[10] and later modified by Davis et al.[9] according to the following reaction

$$NaH + Et_3N \cdot BD_3 \rightarrow NaBD_3H + Et_3N$$

An amount of 0.98 g (40.8 mmol) of premilled NaH (Aldrich, 95%) was mixed with 1.5 equiv of synthesized[11] $Et_3N \cdot BD_3$ (7.1 g, 60.1 mmol) under an argon atmosphere. The suspension was vigorously stirred under reflux at 100 °C for 1 h, at 120 °C for another hour, and afterward at 145 °C for an additional 6 h. The mixture was then cooled down to room temperature, and 50 mL of hexane was added to the suspension, which was stirred overnight. The reaction mixture was filtered off through a fine-grad glass frit, washed with *n*-hexane, and dried under vacuum at various stages: 150 °C/2 h; 180 °C/2 h; 200 °C/12 h. The yield was 69% with respect to NaH (1.15 g). No C or N was detected by elemental analysis.

High-energy ball milling of NaH was carried out by a Fritsch P6 planetary mill at 600 rpm during 1 h using an 80 mL stainless steel vial and balls. The ball-to-powder ratio was approximately 20:1.

Powder X-ray diffraction patterns (see Supporting Information) were obtained with a Philips X'PERT diffractometer, with Cu Kα radiation, 2 kW, with an X'Celerator RTMS detector and automatic divergence slit. The powder was measured on a Si single crystal and sealed in the glovebox by an airtight hood made of Kapton foil, the foil being mounted out of the focus of the spectrometer.

NMR spectra were obtained in both 1 M $NaOH/H_2O$ and $NaOD/D_2O$ solutions on a Bruker 500 MHz instrument at room temperature. The proton, deuterium, and boron spectra were recorded using a 500 ^1H Larmor frequency spectrometer. The spectral windows were 400 ppm for the boron spectrum and 20 ppm for both the ^1H and ^2H spectra. The number of points was set to 4k for the deuterium and boron spectra and 64k for the proton spectrum. The processing involved zero filling but no exponential multiplication.

IR measurements on solids and solutions were obtained using a Specac "Golden Gate" ATR cell in a Biorad Excalibur instrument with a nominal resolution of 1 or 2 cm^{-1}. This ATR cell allows also cooling the sample to −150 °C.

Raman spectra were obtained using a diode pumped solid state laser (488 nm) with a Kaiser Optical Instruments Holospec Monochromator and a liquid nitrogen cooled CCD camera. The samples were sealed in glass capillaries. The spectral resolution was 3−4 cm^{-1} for all experiments.

Theoretical Methods

Structural optimization, harmonic frequencies, harmonic IR intensities, and anharmonic quartic force field were performed with the Gaussian 03 program.[12] The treatment of anharmonicity on vibrational transitions and intensities was obtained using a locally developed Fortran 90 code.[13]

Electronic structure calculations were performed at the DFT level using the three-parameter hybrid functional of Becke (B3LYP) [see ref 14 and therein] and a valence double-ζ Pople basis set including diffuse and polarization functions, 6-31+G(d,p). This model chemistry was chosen since it has been previously shown that it yields reliable results for the computation of vibrational properties for borohydride compounds[7] and, more generally, for small organic[15,16] and radical[17] systems for which an average convergence of 10 cm^{-1} is achieved with respect to the experimental results.

The anharmonic vibrational treatment requires the determination of an analytical potential function determined as follows:[18] from a minimum energy structure of a given system, a quartic force field is built in which the third and fourth derivatives are computed by $6N - 11$ (N = number of atoms) numerical differentiation of analytical second derivatives. In the quartic approximation, the potential provided by the Gaussian code is given by

$$V(q_1, ..., q_{3N-6}) = \frac{1}{2}\sum_i \omega_i q_i^2 + \sum_{i,j,k} k_{ijk} q_i q_j q_k + \sum_{i,j,k,l} k_{ijkl} q_i q_j q_k q_l$$

where q_i is the ith dimensionless normal coordinate and ω_i, k_{ijk}, and k_{ijkl} are the harmonic, cubic, and quartic force constants, respectively, expressed in cm^{-1}. Note that only the anharmonic force constants involving the trimode interactions[19] ($k = l$) are determined by numerical differentiation.

Furthermore, the Watson Hamiltonian, considering a nonrotating system, is used[20]

$$\frac{\hat{H}}{hc} = \frac{1}{2}\sum_i \omega_i p_i^2 + V(q_1, ..., q_{3N-6}) + \sum_\alpha B_\alpha P_\alpha^2$$

where q_i and p_i are, respectively, the dimensionless normal coordinates and their conjugate momenta. The last term represents the major component of the rotational contribution to the anharmonicity.[21]

Then, the vibrational frequencies are evaluated from a variation−perturbation procedure (VCI−P scheme, described in detail elsewhere[22,23]). It is based on a partial diagonalization of the Watson−Hamiltonian matrix representation by taking into account the strongest anharmonic couplings. The procedure provides the anharmonic vibrational energies E_i and the corresponding anharmonic wave functions Ψ_i, from a reliable treatment of Fermi resonances.

Furthermore, this program allows the computation of anharmonic intensities. It requires a quadratic expansion of the dipole surface in which the first and second derivatives of dipole moment, $d_{\alpha i}$ and $d_{\alpha ii}$ (where α is a Cartesian component of the dipole moment vector $d_{\alpha j}$ referred to the Eckart axes), are calculated in an analogous manner to the cubic and quartic force constants detailed above

$$D_\alpha = D_\alpha(0) + \sum_i d_{\alpha i} q_i + \frac{1}{2}\sum_{i,j} d_{\alpha ij} q_i q_j + \frac{1}{6}\sum_{i,j,k} d_{\alpha ijk} q_i q_j q_k$$

The anharmonic intensity between an initial state Ψ_i (generally the zero-point energy state) and a final state Ψ_f is evaluated as previously reported.[24,25]

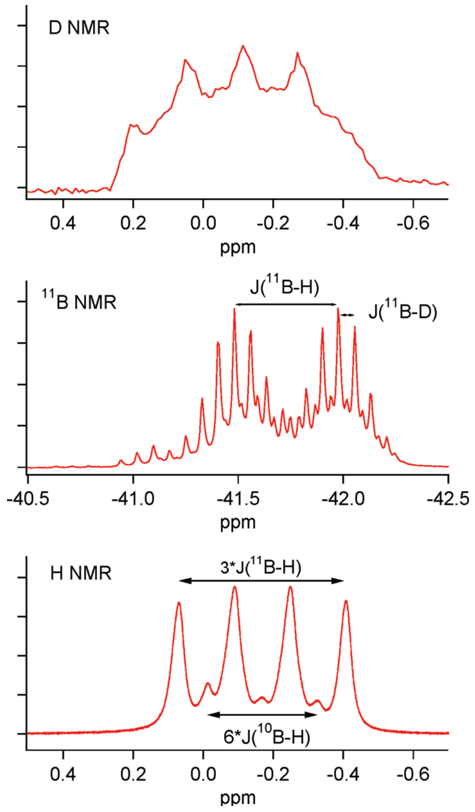

Figure 2. NMR spectra of $NaBD_3H$ in 1 M NaOD/D_2O solution at room temperature.

Results and Discussion

NMR Spectroscopy. Figure 2 presents NMR spectra obtained in 1 M NaOD solution in D_2O. This technique is particularly useful to probe the isotopic purity, as different coupling schemes for different isotopomers can be expected. Previously, statistically distributed isotopic mixtures of borohydrides obtained from exchange reactions in solutions have been studied using NMR.[26] The isotopic purity can be measured quantitatively using ^{11}B NMR. For the BD_3H^- ion, one expects a doublet (due to the ^{11}B,^{1}H scalar coupling) of multiplets with relative intensity 1:3:6:7:6:3:1 because of the $J(^{11}B,^2H)$. The latter coupling is six times smaller because this is the value of the γ^1H/γ^2H ratio.[26] In the experimental spectrum, one also observes a structure due to the $BD_2H_2^-$ ions, at slightly lower field. The signal partially overlaps with the structure of BD_3H^-, but one can observe the structure due to the ^{11}B,^{2}H scalar coupling with relative intensity 1:2:3:2:1, which corresponds to the left line of a triplet due to ^{11}B,^{1}H scalar couplings. On the basis of the relative intensities of the signals, one can estimate that our sample contained approximatively 15% of $BD_2H_2^-$, but no BD_4^-.

In the ^{1}H NMR spectrum, one expects to observe coupling with ^{11}B (four bands) and with ^{10}B (seven bands, natural abundance ca. 20%). Due to the about 3 times smaller magnetogyric ratio of ^{10}B, the spacing between these seven bands is smaller. In the ^{1}H NMR spectrum, one observes (Figure 1) only the outer as well as the central line of these seven bands. The other bands are masked by the stronger lines resulting from the coupling with ^{11}B.

The $^{11}B-^1H$ coupling constant is found (in the ^{1}H and ^{11}B spectra) to be 79.2 ± 0.2 Hz; the $^{10}B-^1H$ coupling constant from the ^{1}H NMR spectra is 26 Hz; and the $^{11}B-^2H$ coupling constant is 11.7 ± 0.2 Hz, in good agreement with the values reported by Smith et al.[26] Further NMR spectra were obtained in 1 M NaOH solution in H_2O. The ^{11}B NMR spectrum is practically identical to the spectrum in the deuterated solvent and confirms previous observations[26,27] that, at least on the time scale of our experiments (2−4 h), the BH_4^- group does not undergo isotopic exchange in alkaline aqueous solution.

Vibrational Spectra. Figure 1 compares the observed IR spectrum of $NaBD_3H$ with those of $NaBH_4$ and $NaBD_4$. In contrast to only two IR active modes expected for the parent

TABLE 1: Experimental Vibrational Frequencies of BD_3H^- [a]

	$NaBD_3H$	$NaBD_3H$	$NaBD_3H$	$RbBD_3H$	
solution	295 K	295 K (lit.)	183 K (IR)	295 K	DFT
2277(IR), 2281(R)	2321(IR), 2331(Ra)	2320	2320	2276(IR)	2283
1693(IR), 1710(Ra)	1710(IR), 1727(Ra), 1765(IR), 1765(sh,Ra)	1727, 1781	1693, 1710, 1767	1683(IR)	1695
1609(IR), 1610(Ra)	1640(IR), 1644(Ra), 1678(sh(IR),wRa)		1641, 1677	1615(IR), 1619(Ra), 1653(Ra)	1639
1061(IR), 1060(Ra)	1083(IR), 1088(Ra), 1063(sh)	1090	1063, 1072, 1083, 1096	1065(IR)	1065
850(IR), 855(Ra)	877(IR), 879(Ra)	855	873, 877, 887		864
800(IR)?	857(IR), 809(w,Ra)	825	854, 864		859

[a] Refs: Davies, R.E.; Kenson, R.E. *Proc. Indiana Acad. Sci.* **1967** (vol. date 1966), *76*, 236−239. Shirk, A.E.; Shriver, D.F. *J. Am. Chem. Soc.* **1973**, *95*, 5901.

TABLE 2: Calculated Harmonic Frequencies (in cm^{-1}) for Isotopic BH_4^- (B3LYP/6-31G(d,p))

	BH_4^-	BH_3D^-	$BH_2D_2^-$	BD_3H^-	BD_4^-
B−H stretching modes	2290 (A_1)	2288 (A)	2286	2283 (A)	
	2283 (T_2)	2283 (E)	2282		
B−D stretching modes		1677 (A)	1695	1695 (E)	1695 (T_2)
			1658	1639 (A)	1639 (A_1)
deformation modes	1239 (E)	1201 (E)	1182	1065 (E)	877 (E)
	1123 (T_2)	1118 (E)	1073	864 (E)	852 (T_2)
		984 (A)	1056	859 (A)	
			934		
			865		

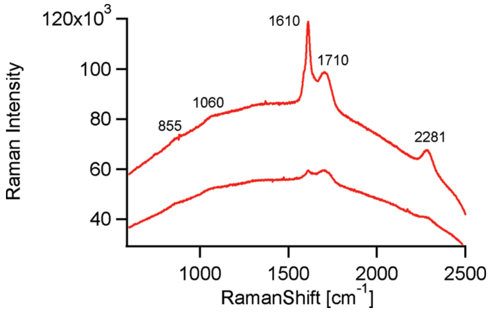

Figure 3. Raman spectra of $NaBD_3H$ in alkaline aqueous solution (parallel and perpendicular polarized).

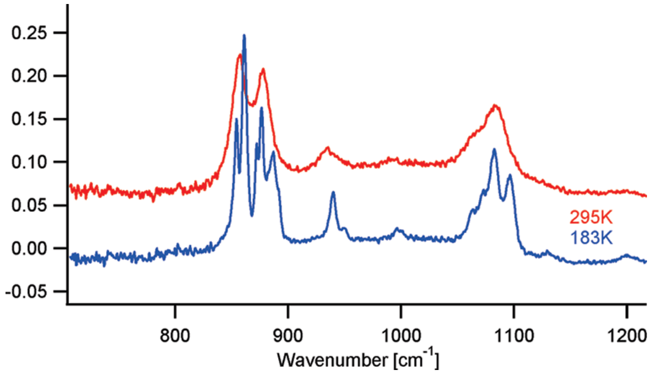

Figure 4. IR spectra of solid $NaBD_3H$ at 295 and 183 K in the deformation mode region.

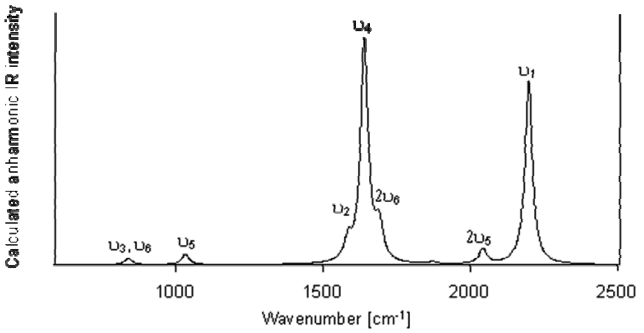

Figure 5. Theoretical anharmonic IR absorption spectrum of BD_3H^-.

tetrahedral compounds, all six vibrational modes of BD_3H^- are both IR and Raman active and are observed in the experimental spectra (Figure 1 and Table 1). Note that a strong single B−H stretching band is observed at 2321 cm^{-1}, with only a very weak second band at ca. 2155 cm^{-1} originating from the Fermi resonance with $2\nu_5$, in contrast to the more complex Fermi resonances seen in the B−D stretching region. Table 1 includes data for $RbBD_3H$ stemming from an accidental exchange reaction during the preparation of $RbBD_4$ (see the Raman spectra (Figure S2 in the Supporting Information)). The weak bands which are seen in Figure 1 at 935, 992, 1063, and 1199 cm^{-1} correspond roughly to the calculated values for the deformation bands of $BH_2D_2^-$ (Table 2) which was shown to be present in the sample by NMR spectroscopy.

IR and Raman spectra were also obtained in 1 M NaOH solution. The corresponding vibrational frequencies are collected in Table 1 (see also Figure S3, Supporting Information, for the IR spectra). Figure 3 shows the Raman spectra of $NaBD_3H$ in basic aqueous solution. The polarized (A symmetry) stretching bands of B−H (2281 cm^{-1}) and of the BD_3 group (1610 cm^{-1}) are shifted to lower frequencies compared to solid $NaBD_3H$ (see Table 1) and are quite similar to the frequencies observed for solid $RbBD_3H$ (see Table 1). Considering the B−D bond lengths measured for $RbBD_4$ (1.206(2) Å)[28] and $NaBD_4$ (1.178(2) Å),[29] one can estimate that the B−D(H) bond length of BD_3H^- in alkaline solution is about 1.20−1.21 Å.

The IR spectra of solid $NaBD_3H$ at 295 and 183 K are shown in Figure 4. It is interesting to note the significant spectral splittings which appear below the structural phase transition. These splittings are much more pronounced than in the low-temperature IR spectra of $NaBH_4$.

Theoretical Calculations. Table 2 collects harmonic frequencies for all isotopic $BH_{4-x}D_x^-$ compounds.

The presence of Fermi resonances in borohydride compounds requires a reliable anharmonic treatment since in this case (i) the anharmonicity is not additive and (ii) IR or Raman intensities arise for overtones and combination bands involved in such a coupling. This excludes the use of scaling factors[30] as well as the use of standard perturbative approach[31] implemented in the most commonly used software for a proper treatment.

The vibrational anharmonic treatment of BD_3H^- with the VCI−P method reveals the presence of mainly three Fermi resonances: $\nu_1^{(A)}$ with $2\nu_5^{(A)}$, $\nu_2^{(A)}$ with $2\nu_6^{(A)}$, and $\nu_4^{(E)}$ with $2\nu_6^{(E)}$. For each, the character of the fundamental in the overtone is slightly higher than 10%. The two components of $2\nu_6$ being very close in energy, the theoretical anharmonic IR spectrum shown in Figure 5 exhibits finally two bands corresponding to the signature of strong anharmonic couplings that occur in this system. The $2\nu_6$ is slightly blue-shifted with respect to the ν_4, in agreement with the picture provided by the experimental investigation, with a relative intensity of about 1:5. The $2\nu_5$ arises at about 150 cm^{-1} lower than ν_1 with a ratio of 1:12, less perceptible on the experimental IR spectrum (Figure 1).

As reported in Table 3 (columns 5 and 6 for the anharmonic positions and intensities, respectively), the computed values of the transitions, by essence in the gas phase, are still far from the experimental data (133 and 55 cm^{-1}, respectively, for ν_1 and ν_2). An attempt to correct these discrepancies was made

TABLE 3: Harmonic and Anharmonic Frequencies (in cm^{-1}) and Harmonic and Anharmonic Intensities (in km·mol^{-1}) for BD_3H^- in the Gas Phase and in Solution (Polarizable Continuum Model)

label	sym	harmonic (gas)	A (ω) (gas)	VCI−P (gas)	A (υ) (gas)	harmonic (solv)	A (ω) (solv)	VCI−P (solv)	A (υ) (solv)	exptl
υ_1	A	2253	449.3	**2144**	360.7	2303	452.3	**2199**	361.1	**2277**
$2\upsilon_5$	A	2053	0.0	**1983**	26.0	2114	0.0	**2044**	30.5	
υ_2	A	1626	67.1	**1555**	39.7	1654	63.9	**1586**	42.1	**1610**
$2\upsilon_3$	A	1655	0.0	**1631**	6.8	1702	0.0	**1678**	9.0	
$2\upsilon_6$	A	1664	0.0	**1641**	46.3	1714	0.0	**1690**	35.2	
υ_3	A	827	1.9	**812**	1.7	851	7.4	**835**	6.1	**850**
υ_4	E	1666	569.1	**1594**	415.6	1708	580.8	**1641**	438.2	**1710**
$2\upsilon_6$	E	1664	0.0	**1645**	37.1	1714	0.0	**1694**	32.7	
υ_5	E	1026	11.8	**1004**	10.8	1057	24.6	**1034**	21.7	**1060**
υ_6	E	832	2.0	**818**	1.8	857	8.2	**843**	7.2	**800**

by modeling the H_2O solvent as a polarizable continuum model (PCM).[32] It has been previously shown[33] that the variant called self-consistent isodensity polarizable continuum model (SCI-PCM)[34] is well suited for vibrational computations. Note that such a model has limitations where nonelectrostatic effects dominate the solute−solvent interaction but save substantial computational time with respect to the consideration of individual molecules. However, the SCI-PCM model improves the anharmonic results by reducing the discrepancies of about 50% providing a theoretical signature in line with its observed counterpart, in addition to the anharmonic treatment.

Conclusions

We have prepared and characterized the selectively isotopically labeled compound $NaBD_3H$. The current results show that the relative intensity of the single B−H stretching mode is strong enough in both IR and Raman spectroscopy to act as a structural probe for individual B−H bonds in complex borohydrides. The anharmonic DFT calculation reproduces well the experimentally observed spectrum (see Figures 1 and 5). In view of future preparations of labeled complex borohydrides, care must be taken to avoid solvents where isotopic exchange has been shown to take place.

Complex borohydrides containing both alkali metal ions as well as transition metal ions can be prepared from alkali borohydrides and transiton metal chlorides using ball milling techniques. Using $NaBD_3H$ in these experiments may give additional structural information on these new compounds.

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Supporting Information Available: Raman spectra of KBH_4 in the stretching mode region, Raman spectra of pure $RbBD_4$ and mixed $RbBD_4$/$RbBD_3H$ at ambient pressure and temperature, IR spectra of $NaBD_3H$ in 1 M NaOH, and X-ray diffraction pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Orimo, S.; Nakamori, Y.; Eliseo, J. R.; Züttel, A.; Jensen, C. M. *Chem. Rev.* **2007**, *107*, 4111.

(2) Miwa, K.; Aoki, M.; Noritake, T.; Ohba, N.; Nakamori, Y.; Towata, S.; Züttel, A.; Orimo, S. *Phys. Rev. B* **2006**, *74*, 155122.

(3) Buchter, F.; Lodziana, Z.; Remhof, A.; Friedrichs, O.; Borgschulte, A.; Mauron, Ph.; Züttel, A.; Sheptyakov, D.; Barkhordarian, G.; Bormann, R.; Chlopek, K.; Fichtner, M.; Sørby, M.; Riktor, M.; Hauback, B.; Orimo, S. *J. Phys. Chem. B* **2008**, *112*, 8042–8048.

(4) Filinchuk, Y.; Rönnebro, E.; Chandra, D. *Acta Mater.* **2009**, *57*, 732.

(5) Aljibury, A. L.; Snyder, R. G.; Strauss, H. L.; Raghavachari, K. *J. Chem. Phys.* **1986**, *84*, 6872.

(6) Renaudin, G.; Gomes, S.; Hagemann, H.; Keller, L.; Yvon, K. *J. Alloys Comp.* **2004**, *375*, 98.

(7) Carbonnière, P.; Hagemann, H. *J. Phys. Chem. A* **2006**, *110*, 9927.

(8) Strauss, H. L. *Acc. Chem. Res.* **1997**, *30*, 37.

(9) Davis, R. E.; Kenson, R. E. *Proc. Indiana Acad. Sci., Volume Date 1966* **1967**, *76*, 236.

(10) Köster, R. *Angew. Chem.* **1957**, *3*, 94.

(11) Kampel, V.; Warshawsky, A. *J. Organomet. Chem.* **1994**, *469*, 15.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(13) VCI−P, a time-independant treatment of anharmonicity from variation−perturbation approches: Carbonnière, P.; Dargelos, A. UMR 5254, Pau, France.

(14) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(15) Carbonnière, P.; Barone, V. *Chem. Phys. Lett.* **2004**, *399*, 226.

(16) Carbonnière, P.; Lucca, T.; Rega, N.; Pouchan, C.; Barone V. *J. Comput. Chem.* **2005**, *26*, 384.

(17) Barone, V.; Carbonnière, P.; Pouchan, C. *J. Chem. Phys.* **2005**, *122*, 224308.

(18) Barone, V. *J. Chem. Phys.* **2005**, *122*, 014108.

(19) Carter, S.; Handy, N. C. *Chem. Phys. Lett.* **2002**, *352*, 1.

(20) Watson, J. K. G. *Mol. Phys.* **1968**, *15*, 479.

(21) Carbonnière, P.; Barone, V. *Chem. Phys. Lett.* **2004**, *392*, 365.

(22) Carbonnière, P.; Dargelos, A.; Adamo, C.; Cioffini, I.; Pouchan, C. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4375.

(23) Carbonnière, P.; Pouchan, C. *Chem. Phys. Lett.* **2008**, *462*, 169.

(24) Baraille, I.; Larrieu, C.; Dargelos, A.; Chaillet, M. *Chem. Phys.* **2001**, *273*, 91.

(25) Burcl, R.; Carter, S.; Handy, N. C. *Chem. Phys. Lett.* **2003**, *380*, 237.

(26) Smith, B. E.; James, B. D.; Peachey, R. M. *Inorg. Chem.* **1977**, *16*, 2057.

(27) Filinchuk, Y.; Hagemann, H. *Eur. J. Inorg. Chem.* **2008**, 3127.

(28) Renaudin, G.; Gomes, S.; Hagemann, H.; Keller, L.; Yvon, K. *J. Alloys Comp.* **2004**, *375*, 98.

(29) Fischer, P.; Züttel, A. *Mater. Sci. Forum* **2004**, *443−444*, 287.

(30) Anderson, M. P.; Uvdal, P. *J. Phys. Chem. A* **2005**, *109*, 2937.

(31) Miller, W. H.; Hernandez, R.; Handy, N. C.; Jayatilaka, D.; Willets, A. *Chem. Phys. Lett.* **1990**, *172*, 62.

(32) Mennucci, B.; Tomasi, J.; Cammi, R.; Cheeseman, J. R.; Frisch, M. J.; Devlin, F. J.; Gabriel, S.; Stephens, P. J. *J. Phys. Chem. A* **2002**, *106*, 6102.

(33) Begue, D.; Carbonnière, P.; Barone, V.; Pouchan, C. *Chem. Phys. Lett.* **2005**, *415*, 25.

(34) Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. *J. Phys. Chem.* **1996**, *100*, 16098.

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