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Computational study of the vibrational spectroscopy properties of boron-hydrogen compounds: $\text{Mg}(\text{B}_3\text{H}_8)_2$, $\text{CB}_9\text{H}_{10}^-$ and $\text{CB}_{11}\text{H}_{12}^-$

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ARTICLE INFO

Article history:

Received 13 January 2017

Received in revised form

1 March 2017

Accepted 8 March 2017

Available online xxx

Keywords:

Boron-hydrogen species

IR

Raman

Vibrational frequencies

Anharmonicity

Density functional theory

ABSTRACT

We report the DFT study of the vibrational spectroscopy properties of $\text{Mg}(\text{B}_3\text{H}_8)_2$, a potential intermediate in the decomposition of $\text{Mg}(\text{BH}_4)_2$, as well as those of $\text{CB}_{11}\text{H}_{12}^-$ and $\text{CB}_9\text{H}_{10}^-$, whose salts can exhibit high ionic conductivities. Because the inclusion of anharmonicity is key to the accurate description of the vibrational properties of BH species [D. Sethio, L. M. Lawson Daku, H. Hagemann. *Int. J. Hydrogen Energy*, 41 (2016) 6814], the calculations were performed both in the harmonic and in the anharmonic approximation. The IR and Raman spectra of $\text{Cs}(\text{CB}_{11}\text{H}_{12})$ and $\text{Na}_2(\text{B}_{10}\text{H}_{10})$ have also been measured. The calculated and experimental spectra are in good agreement. A comparative analysis of the vibrational spectroscopy properties is made for B_3H_8^- and $\text{Mg}(\text{B}_3\text{H}_8)_2$, $\text{B}_{12}\text{H}_{12}^{2-}$ and $\text{CB}_{11}\text{H}_{12}^-$, and for $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{CB}_9\text{H}_{10}^-$.

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Introduction

Boron-hydrogen compounds are receiving a lot of attention for very various reasons. Thus, $\text{Mg}(\text{B}_3\text{H}_8)_2$ and $\text{MgB}_{12}\text{H}_{12}$ are potential intermediates in the decomposition of $\text{Mg}(\text{BH}_4)_2$ [1–8]. On an unrelated note, $\text{Na}(\text{CB}_{11}\text{H}_{12})$, $\text{Na}(\text{CB}_9\text{H}_{10})$ and mixture of both show remarkably high ionic conductivities and stabilities, which make them suitable for use in rechargeable battery application [9–12].

Previous studies have examined the structures, reactivity, the relative stabilities and spectroscopic properties of boron-hydrogen species; see, for instance [13–26], and references therein. Vibrational spectroscopy is a powerful method to

characterize the structure and dynamics of molecular systems. For the boron-hydrogen species, the inclusion of anharmonicity proves to be key for the accurate prediction of their IR and Raman spectra [27].

In this work, we calculate the IR and Raman spectra of $\text{Mg}(\text{B}_3\text{H}_8)_2$ and compare them to those of the free B_3H_8^- ion to assess the influence of the complexation to Mg^{2+} . Similarly, we investigate the differences observed between the IR and Raman spectra of $\text{B}_n\text{H}_n^{2-}$ and $\text{CB}_{n-1}\text{H}_n^-$ ($n = 10$ and $n = 12$) in order to probe the influence of the symmetry breaking induced by the $\text{B} \rightarrow \text{C}$ chemical substitution in closoborane cages. For all calculations, anharmonic effects are included. We have also measured the IR and Raman spectra of $\text{Cs}(\text{CB}_{11}\text{H}_{12})$ and $\text{Na}_2(\text{B}_{10}\text{H}_{10})$.

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<http://dx.doi.org/10.1016/j.ijhydene.2017.03.044>

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Methods

Computational details

All calculations were performed with the Gaussian09 program package [28], using the procedure reported in Ref. [27] for an accurate prediction of the vibrational species of boron-hydrogen species. Thus, the B3LYP functional [29,30] augmented with Grimme's D2 [31] dispersion correction was employed in combination with the large correlation-consistent cc-pVTZ basis. The geometries were optimized using an “ultra-fine” grid and “tight” convergence criteria for the forces and displacements. Vibrational frequencies analyses were then conducted both in the harmonic and in the anharmonic approximation using second-order perturbation theory as implemented in Gaussian09 [32–34].

Experimental details

Cs(CB₁₁H₁₂) was purchased from Katchem and used without any further purification. The FTIR spectrum was measured using a Biorad Excalibur Instrument equipped with a Specac Golden Gate heatable ATR setup at room temperature. The spectral resolution was set to 1 cm⁻¹. Raman spectrum was recorded using 488 nm excitation and a Kaiser Optical HoloSpec monochromator equipped with a liquid nitrogen cooled CCD camera.

Results and discussion

B₃H₈⁻ is a fluxional ion which is formed as an intermediate during the reversible dehydrogenation of Mg(BH₄)₂ and

Y(BH₄)₃ [35–37]. The interconversion between its possible different forms occurs by hydrogen migration [38]. In this study, we consider the most stable conformer of B₃H₈⁻ and compare its vibrational properties to those of the complex Mg(B₃H₈)₂.

Fig. 1 shows the most stable conformer of B₃H₈⁻ as well as Mg(B₃H₈)₂. B₃H₈⁻ in its most stable form is of C_{2v} symmetry and has two B-H-B bridges (Fig. 1a). This form is preserved for the B₃H₈⁻ moieties of the complex Mg(B₃H₈)₂, which is of C_{2h} molecular symmetry. However, due to the coordination to Mg²⁺, the B-H bond lengths for the outer H atoms (H_o) are shorter (1.185–1.188 Å) than those involving the inner (H_i) and bridging (H_b) hydrogen atoms (B-H_i = 1.223–1.229 Å, B-H_b = 1.255–1.469 Å). Fig. 2 compares the calculated IR and Raman spectra of Mg(B₃H₈)₂ with those of B₃H₈⁻, which we previously reported [27].

Upon coordination to Mg²⁺, the B-H_t (H_t: terminal H atoms) stretching modes of B₃H₈⁻ around 2500 cm⁻¹ are split into B-H_o and B-H_i stretching modes. The frequencies of the B-H_o stretching modes are larger than those of the B-H_i stretching modes. The B-H_o stretching modes are found around 2550 cm⁻¹, while the B-H_i stretching modes are found between 2200 cm⁻¹ and 2300 cm⁻¹. One also notes that the B-H_b stretching modes have lower frequencies than the B-H_o and B-H_i stretching modes: these modes are indeed found around 2150 cm⁻¹. Table 1 summarizes the lengths and the associated anharmonic stretching frequencies of the different types of B-H bonds found in B₃H₈⁻ and in Mg(B₃H₈)₂. Its inspection shows that the B-H bond lengths and stretching frequencies in B₃H₈⁻ are both significantly influenced by the coordination to Mg²⁺, and that the stretching frequency is larger the shorter the B-H bond. This observed correlation provides us with a

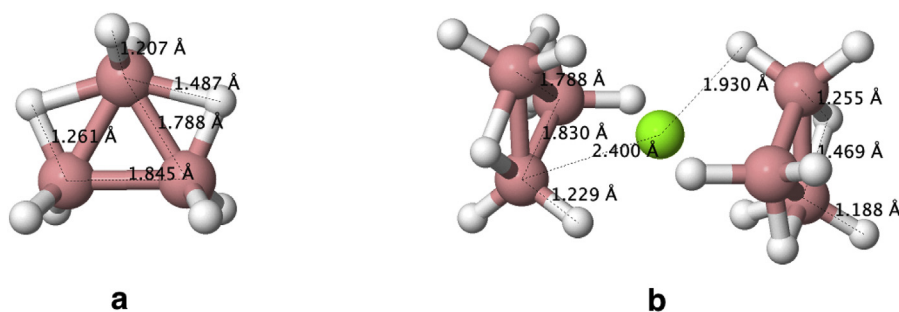


Fig. 1 – The most stable conformer of B₃H₈⁻ ion (a) and the complex Mg(B₃H₈)₂ (b).

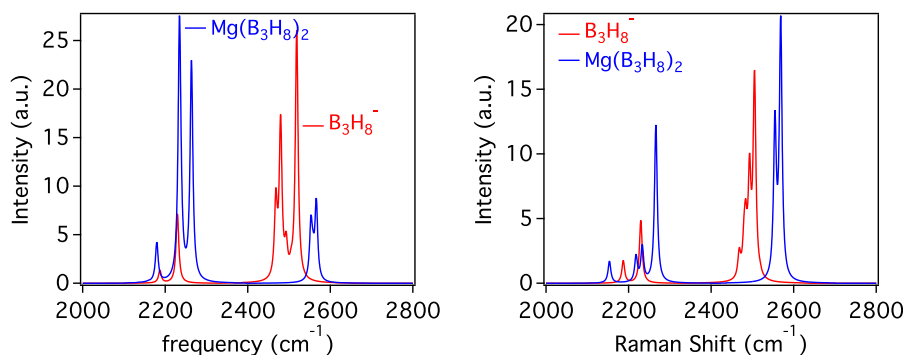


Fig. 2 – Calculated anharmonic IR (left) and Raman (right) spectra of B₃H₈⁻ [27] and Mg(B₃H₈)₂.

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