Computational study of the vibrational spectroscopy properties of boron-hydrogen compounds: Mg(B₃H₈)², CB₉H₁₀ and CB₁₁H₁₂

Daniel Sethio, Latévi Max Lawson Daku *, Hans Hagemann **

Faculty of Sciences — University of Geneva, Quai Ernest Ansermet 30, 1211 Geneva, Switzerland

** Article Info

Article history:
Received 13 January 2017
Received in revised form 1 March 2017
Accepted 8 March 2017
Available online 31 March 2017

Keywords:
Boron-hydrogen species
IR
Raman
Vibrational frequencies
Anharmonicity
Density functional theory

** Abstract

We report the DFT study of the vibrational spectroscopy properties of Mg(B₃H₈)², a potential intermediate in the decomposition of Mg(BH₄)₂, as well as those of CB₁₀H₁₀ and CB₁₁H₁₂, 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 Cs(CB₁₁H₁₂) and Na₂(B₁₀H₁₀) have also been measured. The calculated and experimental spectra are in good agreement. A comparative analysis of the vibrational spectroscopy properties is made for B₃H₈ and Mg(B₃H₈)², B₁₀H₁₀ and CB₁₁H₁₂.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Boron-hydrogen compounds are receiving a lot of attention for very various reasons. Thus, Mg(B₃H₈)² and MgB₁₂H₁₂ are potential intermediates in the decomposition of Mg(BH₄)₂ [1–8]. On an unrelated note, Na(CB₁₁H₁₂), Na(CB₁₀H₁₀) 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 Mg(B₃H₈)² and compare them to those of the free B₃H₈ ion to assess the influence of the complexation to Mg²⁺. Similarly, we investigate the differences observed between the IR and Raman spectra of B₁₀H₁₀ and CB₁₀H₁₀ (n = 10 and n = 12) in order to probe the influence of the symmetry breaking induced by the B → C chemical substitution in closoborane cages. For all calculations, anharmonic effects are included. We have also measured the IR and Raman spectra of Cs(CB₁₁H₁₂) and Na₂(B₁₀H₁₀).

* Corresponding author.
** Corresponding author.
E-mail addresses: max.lawson@unige.ch (L.M. Lawson Daku), hans-rudolf.hagemann@unige.ch (H. Hagemann).
http://dx.doi.org/10.1016/j.ijhydene.2017.03.044
0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.
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 borohydrogen 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

B\(_3\)H\(_8\) is a fluxional ion which is formed as an intermediate during the reversible dehydrogenation of Mg(BH\(_4\))\(_2\) and Y(BH\(_4\))\(_3\) [35–37]. The interconversion between its possible different forms occurs by hydrogen migration [38]. In this study, we consider the most stable conformer of B\(_3\)H\(_8\) and compare its vibrational properties to those of the complex Mg(B\(_3\)H\(_8\))\(_2\).

Fig. 1 shows the most stable conformer of B\(_3\)H\(_8\) as well as Mg(B\(_3\)H\(_8\))\(_2\). B\(_3\)H\(_8\) in its most stable form is of C\(_2\)\(_v\) symmetry and has two B–H–B bridges (Fig. 1a). This form is preserved for the B\(_3\)H\(_8\) moities of the complex Mg(B\(_3\)H\(_8\))\(_2\), which is of C\(_2\)h molecular symmetry. However, due to the coordination to Mg\(^{2+}\), 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(B\(_3\)H\(_8\))\(_2\) with those of B\(_3\)H\(_8\), which we previously reported [27].

Upon coordination to Mg\(^{2+}\), the B–H\(_i\) (H\(_i\): terminal H atoms) stretching modes of B\(_3\)H\(_8\) around 2500 cm\(^{-1}\) are split into B–H\(_o\) and B–H\(_b\) stretching modes. The frequencies of the B–H\(_o\) stretching modes are larger than those of the B–H\(_b\) stretching modes. The B–H\(_o\) stretching modes are found around 2550 cm\(^{-1}\), while the B–H\(_b\) stretching modes are found between 2200 cm\(^{-1}\) and 2300 cm\(^{-1}\). One also notes that the B–H\(_o\) stretching modes have lower frequencies than the B–H\(_i\) and B–H\(_b\) 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 B\(_3\)H\(_8\) and in Mg(B\(_3\)H\(_8\))\(_2\). Its inspection shows that the B–H bond lengths and stretching frequencies in B\(_3\)H\(_8\) are both significantly influenced by the coordination to Mg\(^{2+}\), 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 B\(_3\)H\(_8\) ion (a) and the complex Mg(B\(_3\)H\(_8\))\(_2\) (b).

**Fig. 2** – Calculated anharmonic IR (left) and Raman (right) spectra of B\(_3\)H\(_8\) [27] and Mg(B\(_3\)H\(_8\))\(_2\).
very good starting point for establishing a quantitative vibrational spectra–structure relations for B3H8-containing molecular species or compounds. Finally, in contrast to the vibrational spectra of B3H8, those of Mg(B3H8)2 show some additional weak bands below 400 cm⁻¹ (see Supporting Information), which are associated to complex motions that can be viewed as combinations of B–H, B–Mg, and B–B bending modes.

Table 1 – The B–H bond lengths and the associated anharmonic stretching frequencies for B3H8 and Mg(B3H8)2 (B3LYP-D2/cc-pVTZ results).

<table>
<thead>
<tr>
<th>Species</th>
<th>r (Å)</th>
<th>v(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3H8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B–H₁</td>
<td>1.207</td>
<td>2367–2399</td>
</tr>
<tr>
<td>B–H₈</td>
<td>1.261–1.487</td>
<td>2058–2131</td>
</tr>
<tr>
<td>Mg(B3H8)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B–H₁</td>
<td>1.185–1.188</td>
<td>2553–2568</td>
</tr>
<tr>
<td>B–H₈</td>
<td>1.225–1.229</td>
<td>2218–2266</td>
</tr>
<tr>
<td>B–H₈</td>
<td>1.255–1.469</td>
<td>2153–2180</td>
</tr>
</tbody>
</table>

* Ref. [27].

Fig. 3 – Comparison of the calculated anharmonic Raman spectrum of CB₁₁H₁₂ with the experimental room-temperature Raman spectrum of Cs(CB₁₁H₁₂) (left), and comparison of the experimental Raman spectra of B₁₂H₂₂ [27] and CB₁₁H₁₂ (right).

Fig. 4 – Comparison of the experimental Raman (Top) and IR (Bottom) spectra Cs(CB₁₁H₁₂) with the calculated harmonic and anharmonic Raman (Top) and IR (Bottom) spectra of CB₁₁H₁₂.

In order to illustrate the importance of including anharmonicity in the vibrational analyses of BH species, we compare in Fig. 4 the experimental Raman and IR spectra of Cs(CB₁₁H₁₂) with the calculated harmonic and anharmonic ones of CB₁₁H₁₂. In the bending mode region below 1200 cm⁻¹, the harmonic Raman spectrum already shows a satisfactory agreement with experiments, the inclusion of anharmonicity bringing small though noticeable changes to the predicted spectrum. The IR spectra are plotted between 2000 cm⁻¹ and 3250 cm⁻¹ in the stretching mode region. In
The inclusion of anharmonicity proves to be key to the accurate description of the B–H and C–H stretching modes, whose frequencies are otherwise noticeably overestimated.

As this can be inferred from the comparison in Fig. 5 of the IR and Raman spectra of CB9H10 and B10H10, the B → C substitution in B10H10 lead to similar trends in the vibrational spectra. The symmetry is lowered from D_{2h} to C_{2v}: the IR active modes transforming as E_1 and E_2 become E and A_1, respectively, and the Raman active modes transforming as E_3 become E while those of A_2 symmetry remain A_2 in C_{2v}.

For B10H10 and B12H12, the substitution of one boron atom by a carbon atom translate into a blue shift of the most intense bands of their Raman spectra between 550 cm\(^{-1}\) and 1200 cm\(^{-1}\) (see Supporting Information). Such a blue shift is also observed for the IR or Raman bands associated to the B–H stretching modes (see Fig. 5 and Supporting Information), and the C–H stretching modes are observed at 3071 and 3087 cm\(^{-1}\) for CB11H12 and CB9H10, respectively. The lengths of the B–H and C–H bonds in CB9H10, B10H10, B11H12 and B12H12 as well as the associated stretching frequencies are summarized in Table 2.

The inspection of Table 2 shows that the B → C substitution in B10H10 and in B12H12 leads to a ~0.01 Å shortening of the B–H bonds, hence to a strengthening of these bonds, and concomitantly to a large increase of the stretching frequencies. One also notes that the C–H bond is predicted to be slighly larger in CB11H12 than in CB9H10, which is the reverse of the order observed for the C–H stretching frequencies.

### Concluding remarks

We have performed a detailed DFT study of the vibrational spectroscopy properties of Mg(B3H8)2, CB9H10 and B10H10, with the inclusion of anharmonic effects. We have also measured the IR and Raman spectra of CB11H12 in Cs(CB11H12) and B10H10 in Na[B10H10]. A very satisfactory agreement has been observed between the calculated and experimental spectra. The results obtained for Mg(B3H8)2 and CB9H10 (n = 10 and n = 12) have been compared to those previously reported for B10H10 and B12H12 (n = 10 and n = 12), respectively [27]. For B3H8 and Mg(B3H8)2, the comparative analysis helped evidence the influence of the binding to Mg\(^{2+}\) on both the structural and vibrational properties of B3H8. For BnH2n+ (n = 10 or n = 12), the B → C substitution was shown to give rise to the shortening of the B–H bonds, which is accompanied by a large increase of the B–H stretching frequencies, and to the expected appearance of a C–H stretching band at 3071 cm\(^{-1}\) and at 3087 cm\(^{-1}\) for CB9H12 and CB9H10, respectively.

The vibrational frequencies reported in this study correspond to fundamental vibrational frequencies. Interestingly however, a preliminary analysis suggests that the overtones and combination bands cannot be fully neglected for Mg(B3H8)2. The importance of the nonfundamental transitions in the vibrational spectra of boron-hydrogen species will be addressed in a future study.

### Acknowledgment

This work was supported by the Swiss National Science Foundation (grant no. 200020_156681).

### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2017.03.044.
REFERENCES


