



Vibrational spectra and structure of borohydrides



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ARTICLE INFO

Article history:

Available online 9 February 2013

Keywords:

Hydrogen storage
Vibrational spectra
Borohydrides
FG method

ABSTRACT

A comparison of the vibrational spectra of many inorganic borohydrides allows us to distinguish compounds with isolated BH_4^- ions and compounds containing complex ions such as $\text{Sc}(\text{BH}_4)_4^-$. The characteristic spectral features of both types of compounds are identified, showing that the B–H bonding is quite different in both cases. A detailed analysis of the vibrations of the isolated BH_4^- ions provides new information about their local structure. Angular deformations of individual borohydride ion are analyzed quantitatively. It appears that the compounds containing isolated BH_4^- ions belong to those with the most electropositive cations and the highest decomposition temperature, while the complex borohydrides show significantly lower decomposition temperatures and possible diborane formation.

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1. Introduction

Inorganic borohydrides are actively studied as hydrogen storage materials. In this context, Nakamori et al. [1] showed that there is a relation between the decomposition temperature of the borohydride and the Pauling electronegativity of the cation involved. This has led to the synthesis and characterization of many new mixed metal borohydrides with the aim to tune the decomposition temperature by the combination of a very electropositive ion (e.g. Li^+) with for instance a transition metal ion (Zn^{2+}) (e.g. [2–4] and references therein). In a recent paper, Callini et al. [5] have noted a correlation between the splitting of the B–H stretching mode region (as observed by Raman spectroscopy) and decomposition temperature in relation also to diborane release. Chemically, it seems quite reasonable to that highly electropositive ions form ionic solids with isolated BH_4^- groups, while less electropositive ions will form complexes. The intensity changes observed in the IR spectra for these complex borohydride ions in the bending mode region reveal new interactions between the B–H bond and metal atom.

Several reviews of vibrational spectra of borohydrides have been published (see e.g. [6,7]). However, for compounds with complex ions such as $\text{Li}_2\text{Zn}(\text{BH}_4)_5$, the thermal decomposition can lead to the formation of diborane, in addition to Hydrogen.

In the course of our studies in this field, we have obtained vibrational spectra of many new borohydride compounds. The comparison of these data shows that one can separate the compounds in two categories. The corresponding spectral characteristics are highlighted and discussed. Further analysis, using the FG method,

shows that for individual BH_4^- ions, small angular deformations can result in significant spectral changes.

2. Experimental and theoretical methods

IR spectra on laboratory prepared and purified CsBH_4 [8] and $\text{Ca}(\text{BH}_4)_2$ were obtained using a Specac ATR setup and a Biorad Excalibur FT-IR instrument.

Computational studies were performed within Density Functional Theory (DFT), and consisted in the optimization of the structures of isolated NaBH_4 molecule and of BH_4^- ion and in the calculation of their vibrational spectra in the harmonic approximation. The calculations were performed with the B3LYP functional [9,10] and 6–31g(dp) basis set of triple-zeta polarized quality for Boron and Hydrogen atoms, using the Gaussian program package [11].

3. Results and discussion

As we previously reported for various systems, the calculated spectra are in good agreement with experimental data [4,12,13].

Fig. 1 compares calculated IR spectra for a selection of different compounds. The isolated BH_4^- ion with tetrahedral symmetry has two triply degenerate IR active modes which are found at ca 2300 cm^{-1} (B–H stretching) and ca 1100 cm^{-1} (B–H bending). Experimental spectra with BH_4^- having a local T_d symmetry show in the B–H stretching mode region more bands caused by strong Fermi resonances, which are generally spread over ca 100 cm^{-1} , as observed for the solid alkali borohydrides [6,14]. The calculated spectrum of the molecular NaBH_4 model presents two well separated stretching bands which are due to different length of the B–H bonds, one B–H bond length of 1.204 \AA and three B–H lengths of 1.246 \AA . In this system of C_{3v} symmetry, the BH_4^- unit has a C_{3v} symmetry, with three Hydrogen atoms pointing to the Na^+ ion and the other one in the opposite direction; the longer B–H distance corresponds to the Hydrogen atoms close to the metal ion.

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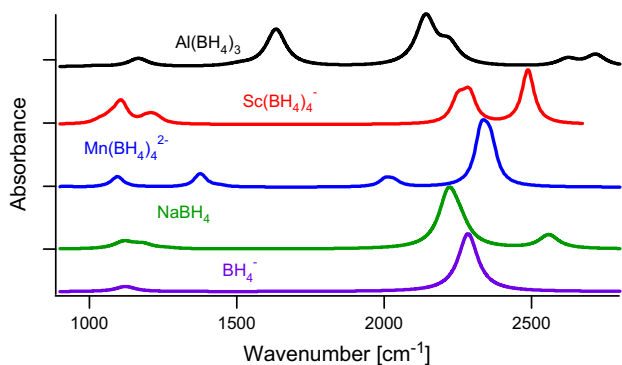


Fig. 1. DFT calculated IR spectra for different borohydrides systems. The calculations were performed on single ion/molecule. The spectra of $\text{Mn}(\text{BH}_4)_4^{2-}$, $\text{Sc}(\text{BH}_4)_4^-$ and $\text{Al}(\text{BH}_4)_3$ are from Refs. [15,4,13], respectively.

Similar splitting of the B–H stretching bands are also observed in the spectra of other molecular model complexes in Fig. 1 and can be associated with different B–H bond lengths in these compounds (the B–H bond oriented towards the central metal is longer than the B–H bonds at the outer side of the complex). Experimental data both from IR and Raman data confirm these theoretical results [3,4,12,13].

The spectra in Fig. 1 show quite different features in the bending mode region. For BH_4^- and NaBH_4 , the relative intensity of the bending and stretching modes remains similar, while this is not the case for the other compounds. For $\text{Al}(\text{BH}_4)_3$ [13] and $\text{Mn}(\text{BH}_4)_4^{2-}$ [15], the bending mode (which is IR-forbidden in tetrahedral symmetry) becomes very strong and is shifted towards higher frequencies. In these two cases, the borohydride ion has a bidentate binding towards the central metal atom. The bending of the inner BH_2 unit moves the hydrogen atoms towards the metal. In this case, the vibrational wavefunction receives also some metal–hydrogen stretching contributions, which have strong IR intensity. Consequently, the relative IR intensity of this mode increase strongly with increasing interaction with the central metal atom. For tridentate binding, as in $\text{Sc}(\text{BH}_4)_4^-$ [4,12], the IR intensity of the umbrella bending mode (observed typically around 1200 cm^{-1}) of the BH_3 group pointing towards the metal increases by a similar coupling with the metal. These observations show qualitatively that for complexes such as $\text{Mn}(\text{BH}_4)_4^{2-}$ and $\text{Sc}(\text{BH}_4)_4^-$, the central metal influences the B–H bonds.

Contrarily to the trend discussed above for the complex ions, the B–H stretching bands remain well grouped (within 100 cm^{-1}) in the experimental spectra of alkali borohydrides and in those of $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$. In this case, one can consider that the borohydride ion remains isolated and is only subject to small deformations caused by the surrounding ions. One can thus use group theory considerations to analyze the local symmetry of the borohydride ion. Periodical DFT calculations performed on several systems (e.g. LiBH_4 [16,17]) have shown that the factor group splitting remains typically quite small (within ca 10 cm^{-1}), so that one can use the site symmetry in the crystal to predict the splitting of the deformation modes.

Fig. 2 presents the experimental bending mode region of the IR spectra of three compounds. In CsBH_4 , the borohydride ion has tetrahedral symmetry, thus only one IR active band is observed. Upon lowering the site symmetry (LiBH_4 : C_s , $\text{Ca}(\text{BH}_4)_2$: C_2), one observes the splitting of the initially triply degenerate deformation mode and the appearance (as weak bands) of the components of the doubly degenerate E mode which was forbidden in tetrahedral symmetry.

However, while the analysis of the splitting provides information about the site symmetry, there is no quantitative information

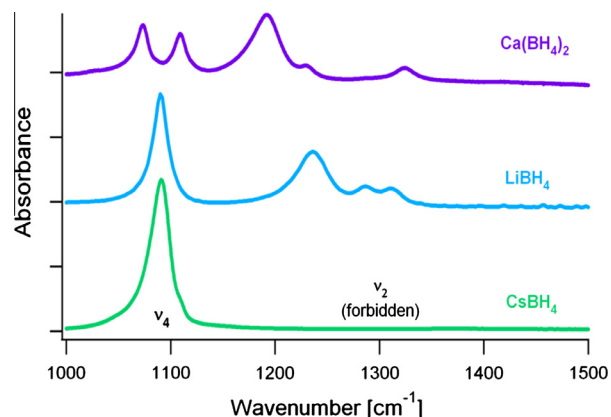


Fig. 2. Experimental IR spectra at room temperature in the bending mode region.

about the extent of the deformation. For this reason, we have started a detailed vibrational analysis of the borohydride ions using the FG method [18]. In this method, the vibrations are described in terms of coordinates of internal stretching and bending displacements, and the force constant matrix F contains not only stretching and bending terms, but also stretch–stretch, stretch–bend and bend–bend interaction terms.

In our approach, we have obtained the F matrix from the vibrational analysis performed on the optimized geometry of BH_4^- in T_d . We have constructed the G matrix, which depends on atomic masses and bond lengths and angles. Then, starting from the relaxed geometry of T_d symmetry, we make small angular variations (in the G matrix) and recalculate the vibrational frequencies with the same F matrix. The results for small deformations of 4° in different directions are shown in Fig. 3.

Fig. 3 shows that for the deformations leading to D_{2d} symmetry, the E mode shows a large splitting. In the case of the deformation leading to C_{3v} symmetry, the splitting of the T_2 mode is of the order of 100 cm^{-1} for a 4° deformation. It is interesting to note that the experimental spectrum observed for LiBH_4 (see Fig. 2) presents a similar splitting. In this case, however, the E mode is also split, as the site symmetry is C_s . However, this splitting disappears at the orthorhombic to hexagonal phase transition, while the splitting of the T_2 mode remains nearly unchanged. This observation shows that in fact the local symmetry of the BH_4^- ion in the orthorhombic

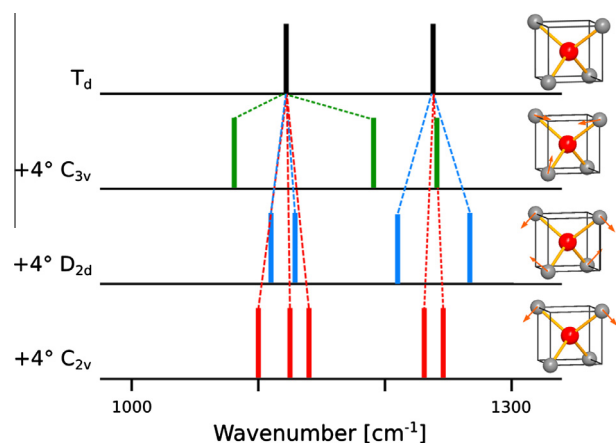


Fig. 3. Splitting of the bending modes, ν_4 (low frequency mode) and ν_2 (high frequency mode), with the distortion of the BH_4^- ion from the tetrahedral symmetry. In T_d symmetry, ν_4 is the triple degenerate mode (T_2) and ν_2 is the double degenerate one (E). The splitting of the modes is calculated by using the FG approach.

phase is quite close to a C_{3v} symmetry. Similarity of local structure may also be related to the group–subgroup relations of the different space groups observed for $LiBH_4$ as analyzed by Dmitriev et al. [19].

4. Conclusions

The comparison of many experimental and theoretical vibrational spectra of inorganic borohydrides shows that one can classify the compounds in different categories: compounds with isolated BH_4^- ions (e.g. $LiBH_4$), and complex ions with either tridentate (e.g. $Sc(BH_4)_4^-$) or bidentate (e.g. $Zn(BH_4)_3^-$) orientation of the borohydride to the central metal atom. Spectral characteristics for all categories have been presented. For compounds with isolated BH_4^- ions, it has been shown that small angular variations may lead to important changes in the spectra.

Acknowledgement

This work is supported by the Swiss National Science Foundation.

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