

# Relating structure and spectroscopic properties of borohydride species from $\text{BH}_4^-$ to $\text{B}_{12}\text{H}_{12}^{2-}$ .

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## Short summary

Vibrational spectroscopic properties of borohydride species are presented based on both experimental data and theoretical DFT calculations. In particular, the vibrational properties of individual  $\text{BH}_4^-$  ions in solids as well as of complex ions such as  $\text{Sc}(\text{BH}_4)_4^-$  are discussed. Spectroscopic properties of  $\text{B}_{12}\text{H}_{12}^{2-}$  in relation to its local symmetry in the solid phase are presented.

## Long summary

Borohydrides have been proposed as potential hydrogen storage materials, leading to an intensive research effort on new mixed metal borohydride containing compounds. Generally speaking, these compounds can be divided into two categories. In the first one, borohydrides appear in the crystal as individual species. In this case, the local symmetry (site group) can be related to the splittings observed in the vibrational spectra for the deformation modes. The extent of the deformations can be quantitatively estimated using the GF method [1]. This approach allows also to estimate B-H bond length changes in a series of compounds with similar structures.

In the second category, complex ions such as  $\text{Sc}(\text{BH}_4)_4^-$  or  $\text{Zn}_2(\text{BH}_4)_5^-$  are formed, leading to significant splitting of the B-H stretching modes, as well as to spectral signatures related to the bidentate or tridentate binding towards the metal ion. An IR database of a collection of samples has been assembled [2].

Temperature dependent experiments can reveal position and bandwidth changes which can be associated to dynamic behaviour and/or structural phase transitions.

Spectroscopic properties of borohydride species can be predicted using DFT methods. During the thermal decomposition of borohydrides, intermediate species such as  $\text{B}_3\text{H}_8^-$  and  $\text{B}_{12}\text{H}_{12}^{2-}$  can be formed. In order to achieve a good agreement for vibrational spectra, anharmonic calculations have to be performed. This has been done for a series of species from  $\text{BH}_3$  to  $\text{B}_{12}\text{H}_{12}^{2-}$  and compared to available literature data [3].

The dodecaboranes  $\text{B}_{12}\text{H}_{12}^{2-}$  have attracted recent interest in the field of ionic conduction. As the symmetry of this icosahedral ion is systematically lowered in any crystal phase (which does not allow five-fold rotation axes), selection rules are changed from one phase to the other. This has recently been documented for the mixed crystal ionic conductor  $\text{LiNaB}_{12}\text{H}_{12}$  [4]. Further, the effect of substitutions of hydrogen by halogens will be discussed [5].

## References:

[1] Quantitative Spectra–Structure Relations for Borohydrides V. D’Anna, L.M. Lawson Daku and H. Hagemann *J. Phys. Chem. C*, 119 (38) (2015), p21868-21874.

[2] FTIR spectra of inorganic borohydrides. V. D’Anna, A. Spyratou, M. Sharma and H. Hagemann *Spectrochimica Acta, Part A* 128 (2014), p902-906.  
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[3] D. Sethio, L.M. Lawson Daku and H. Hagemann, *Int. J. Hydrogen Energy*, accepted for publication.

[4] Synthesis of a Bimetallic Dodecaborate  $\text{LiNaB}_{12}\text{H}_{12}$  with Outstanding Super Ionic Conductivity. L. He, H.-W. Li, H. Nakajima, N. Tumanov, Y. Filinchuk, S.-J. Hwang, M. Sharma, H. Hagemann and E. Akiba *Chemistry of Materials*, 27 (16) (2015), p5483-5486.

[5] Theoretical study of  $\text{B}_{12}\text{H}_n\text{F}_{(12-n)}^{2-}$  species. M. Sharma, D. Sethio, V. D’Anna and H. Hagemann *Int. J. Hydrogen Energy*, 40 (37) (2015), p12721-12726.

