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Vibrational spectroscopy and DFT calculations of hydrogen containing compounds

Hans Hagemann, Département de Chimie Physique, Université de Genève

Summary

Vibrational spectroscopy is a universal tool to probe structure and bonding in molecules and crystals. The interpretation of the spectra is not always straightforward. Modern theoretical DFT calculations on isolated ions or molecules as well as on periodical systems show excellent agreement with experiment and contribute to the understanding of the materials studied. Our research focusses on the fundamental understanding of bonding properties in selected systems, in particular on the boron-hydrogen bond.

In the search of new potential hydrogen storage materials, it is not always easy to establish the position of the hydrogen atoms in new compounds using diffraction methods alone. In this presentation, we illustrate a combined theoretical and spectroscopical approach to investigate spectra-structure relationships for different hydrogen containing systems. These studies are complementary to synchrotron X-ray diffraction as well as neutron diffraction experiments.

After showing results on A_2MH_6 compounds (A = Mg, Ca, Sr, M =Fe, Ru), we adress in more detail compounds with BH_4^-. A general approach using the FG method developped by Wilson, Decius and Cross allows to associate small splittings quantitatively to spectific angular deformations of the tetrahedral ion. Further, a linear relation between bond length and vibrational frequency is obtained for the BH_4^- ion in a series of cubic crystals. Several new compounds which have been prepared in the last 6 years contain complex ions such as $Sc(BH_4)_4^-$. DFT calculations on these isolated ions and comparison with vibrational spectra show that these ions keep their structure also in the solid state.

Temperature and/or pressure dependent experiments can lead to structural phase transitions or chemical reactions which are probed by vibrational spectroscopy. In particular, we have adressed the isotope exchange reactions between $M(BH_4)_2$ (M=Mg,Ca) with D_2 gas at pressures up to 80 bar and temperatures up to 200°C, which is quite lower that the previously reported temperatures for isotope exchange in the alkali borohydrides. These experiments show that the exchange reaction is reversible and allow to estimate the corresponding activation energy.

More recently, we have initiated experiments to study intermediate products formed during the thermal decomposition of borohydrides, and some initial results will be shown as an illustration for our future research in this field.