Quantitative Spectra—Structure Relations for Borohydrides

Vincenza D’Anna,*†‡ Latévi Max Lawson Daku,* † and Hans Hagemann‡

†Département de chimie physique, Sciences II, Université de Genève, 30, Quai Ernest-Ansermet CH-1211 Genève 4, Switzerland
‡CNRS, 46 Allee Italie, F-69364 Lyon 07, France

Supporting Information

ABSTRACT: Among the different potential hydrogen storage materials, borohydrides have been largely investigated because of their high gravimetric and volumetric hydrogen content. In the analysis of borohydrides, vibrational spectroscopy plays an important role since it gives information on the local structure of the BH4− ion inside the solid. Here the GF method, developed by Wilson, is used in order to determine the local symmetry of BH4− in solid borohydrides starting from their vibrational spectra. Two different cases of deformations of BH4− are considered. In the first case, the effects of small angular variations on the vibrational spectra of borohydrides will be taken into account; starting from the splitting of the bands corresponding to the deformation modes, the angular deformations will be estimated. In the second one, the BH4− under chemical pressure (in different cubic alkali halides) is considered; in this case, the symmetry of the BH4− remains Td while the bond lengths change according to the pressure experienced. Different practical examples will be illustrated.

INTRODUCTION

With the perspective to find an alternative to the “oil” economy, the use of hydrogen is quite promising because of its high weight energy content1 and the negligible environmental impact of its oxidation.2 However, the problem related to the storage of hydrogen in vehicles is one of the main obstruction to the transition to the “hydrogen economy”.3 In order to overcome this problem, several research projects have been devoted to find materials suitable to store hydrogen at conditions of temperature and pressure practically achievable. All the characteristics of a practical usable hydrogen storage material are summarized in the directives of the U.S. Department of Energy (DOE);4 presently, there are no materials that fulfill the DOE requirements.1,5,6 Among the potential hydrogen storage materials, borohydrides have been largely investigated because of their high gravimetric and volumetric hydrogen content (see, for example, ref 7 and references therein).

Spectroscopic techniques like NMR and vibrational spectroscopy can contribute to describe the local structure in a given system. This is particularly useful in the case of hydrogen-containing compounds, where powder X-ray diffraction is inherently not the best method to localize accurately the hydrogen atoms.

Group theory predicts the splittings of vibrational bands expected upon lowering the symmetry of a tetrahedral ion into a given crystal. However, the magnitude of these splittings is not predicted.

In this work, we apply the well-known GF method8 for vibrational spectroscopy to study the effect of small angular deformations on the tetrahedral BH4− ion. In the second part, we study the effect of bond length change on the vibrational frequencies in tetrahedral symmetry. Within the GF approach, the frequencies are calculated from the solution of the secular equation relating the force constant matrix (F) and the matrix containing information about the geometry and the atomic masses of the system (G):

$$|GF - I\lambda| = 0$$

(1)

where I is the identity matrix and \( \lambda \) is related with the vibrational frequencies (\( \nu \)):

$$\lambda = 4\pi^2\nu^2$$

(2)

The initial force field used results from a DFT calculation on an individual BH4− ion, while historically the force field was often parametrized from experimental data. Different theoretical calculations lead obviously to different force matrices and different vibrational frequencies. However, as will be shown in this paper, the magnitudes of the splittings of the degenerate modes upon deformations are very similar. A further matter of concern is the effect of anharmonicity and Fermi resonances. In a previous paper,9 we studied in detail the Fermi resonances observed in the cubic alkali borohydrides and deuterides. Significant differences between harmonic and anharmonic frequencies were observed. In order to take indirect account of these effects, the stretching force constants were adjusted using experimental stretching frequencies to correlate the stretching frequencies with B−H bond length.

In the first part of this study, the force field is kept fixed, and only the G-matrix is changed in order to simulate different

© 2015 American Chemical Society

DOI: 10.1021/acs.jpcc.5b06045
J. Phys. Chem. C 2015, 119, 21868−21874
angular variations and to calculate the resulting vibrational frequencies. These calculated results are compared with the experimental vibrational spectra of LiBH₄ and NaBH₄. In the second part, we first show by comparison with experimental data that only the diagonal B–H stretching force constants change significantly with the bond length. We then will study the evolution of the experimental vibrational spectra of the tetrahedral BH₄⁻ ion in many different cubic crystalline environments.

The approach presented here is general and can be easily applied to other tetrahedral systems such as AlH₄⁻ or extended to other systems with different symmetry (XY₆, X₂Y₃, etc.)

### BACKGROUND: THE GF METHOD FOR TETRAHEDRAL SYSTEM

The GF method⁸ is a classical mechanics¹⁰ method, which allows the description of the small-amplitude vibrations of a molecule about its equilibrium geometry in terms of its normal coordinates. Before going in the detailed derivation of the method for the title molecule, we give a brief overview of the method, while putting the emphasis on the physical meaning of the G and F matrices.

For a molecule of N atoms with n internal degrees of freedom described by the internal coordinates R = (Rᵢ)ᵢ=1,...,n the Lagrangian reads:

\[ L = \frac{1}{2} \sum_{ik} a_{ik}(R) \ddot{R}_i \dot{R}_k - V(R) \]

where \( \dot{X} \) denotes the time derivative of \( X \); \( T(R, \dot{R}) \) is the kinetic energy of the system, without the contributions from the rotational and the translational degrees of freedom; and \( V(R) \) is the potential energy. The coefficients \( a_{ik}(R) \) are given by

\[ a_{ik}(R) = \sum_{j=1}^{N} m_j \frac{\partial x_j}{\partial R_i} \frac{\partial x_j}{\partial R_k} \]

where \( m_i \) is the mass of the \( j \)th atom; \( x_j \), its Cartesian coordinates expressed in terms of the generalized coordinates:

\[ x_j = z_j(R_{1},...,R_{n}) = z_j(R) \]

and where “. . .” denotes the scalar product.

Taking the equilibrium geometry as the origin \( O \) and setting \( V(O) = 0 \), the second-order Taylor series expansions about \( O \) of the kinetics and the potential energy potential energies are given by

\[ T(R, \dot{R}) = \frac{1}{2} \sum_{ik} a_{ik}(O) \dot{R}_i \dot{R}_k \]

\[ V(R) = \frac{1}{2} \sum_{ik} F_{ik} R_i R_k \]

From the Lagrange equations of motion

\[ \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{R}_i} \right) - \frac{\partial L}{\partial R_i} = 0 \]

we obtain the set of n equations

\[ \sum_{k} a_{ik}(O) \ddot{R}_k = \sum_{ik} F_{ik} R_k \]

which can be put in the matricial form

\[ A \ddot{R} = FR \]

with \( A = (a_{ik}(O))_{i,k=1,...,n} \) a symmetric positive-definite matrix \( (T > 0) \) and \( F = (F_{ik})_{i,k=1,...,n} \). Putting \( G = A^{-1} \), the above equation can also be written

\[ \ddot{R} = GF \]

whose solution relies on the determination of the eigenvalues of the GF matrix:

\[ GF = PA \]

\( P \) is the matrix whose columns are the eigenvectors of \( GF \), and \( A = \text{diag}(\lambda_i)_{i=1,...,n} \) the diagonal matrix made of its eigenvalues \( \lambda_i \). We thus see that, for small-amplitudes changes in the internal coordinates about the equilibrium molecular geometry, \( G^{-1} \) and \( F \) help express the kinetic energy and the harmonic potential energy of the internal coordinates, respectively. Setting \( Q = P^{-1} R \), the eigenvalue problem reads

\[ \ddot{Q} = \Lambda Q \]

The columns of \( Q \) are the so-called normal coordinates.

### The G Matrix

According to Wilson,⁸ the first step for the construction of the \( G \) matrix consists in the determination of a relation between the internal and the Cartesian coordinates; the choice of the internal coordinates is convenient since the variations of the internal coordinates correspond to the stretching and bending modes.

The matricial expression of the relation between internal and Cartesian coordinates is given in eq 13:

\[ R = Bx \]

where \( R \) and \( x \) are the internal and Cartesian coordinates vectors, respectively, and \( B \) is the geometry transformation matrix. The linear form of the eq 13 is

\[ R_k = \sum_{i=1}^{3N} B_{ik} x_i, \quad k = 1, 2, ..., 3N - 6 \]

where \( N \) is the number of atoms.

From the \( B \) matrix, it is possible to obtain the \( G \) matrix, since it is defined as the row by row product of the \( B \) matrix weighed by the atomic masses.⁸

\[ G = BM^{-1}B \]

Each element of the \( G \) matrix is, then, expressed as

\[ G_{kl} = \sum_{i=1}^{3N} \frac{B_{ki}B_{li}}{m_i}, \quad k, l = 1, 2, ..., 3N - 6 \]

For 1 ≤ i ≤ 3, \( m_i \) refers to the first atom, for 4 ≤ i ≤ 6, \( m_i \) refers to the second one, et cetera.

In order to apply the procedure of the construction of the \( G \) matrix to a tetrahedral system, the internal and Cartesian coordinates of the equilibrium positions and of the displacements from the equilibrium should be defined; henceforth, everything will be referred to the \( \text{BH}_4^- \) group.

The Cartesian coordinates of the equilibrium positions and of the displacements, with respect to an arbitrary reference system, are summarized in Table 1, while the internal coordinates (10 in total, including 4 bond lengths and 6 angles) at equilibrium positions are shown in Figure 1. Accordingly, \( \Delta r_i \) and \( \Delta \alpha_{ij} \) are the displacement from equilibrium position expressed in terms of internal coordinates and they correspond to the stretching and the bending modes,
The expressions of $\Delta \tau_i$ and $\Delta \alpha_{ij}$ in terms of $x_0, y_0, z_i$ are given in eqs 17 and 18, respectively. All the mathematical procedures are shown in the Supporting Information.

The F Matrix. The force constant matrix was obtained from a calculation on the isolated BH$_4^-$ group within Density Functional Theory (DFT). The calculation was performed using Gaussian 09 package, the B3LYP hybrid functional and the 6-31g(d,p) basis set of valence double-$\zeta$ polarized quality. In this calculation, the symmetry of the BH$_4^-$ was kept $T_d$. The input file was prepared in such a way that the F matrix was expressed in the same internal coordinates as the G matrix. Consequently, also the F matrix is a 10 × 10 symmetric matrix, and shows the stretch–stretch, bend–bend and stretch–bend blocks. The F obtained from Gaussian calculations is shown in the Supporting Information.

In the first part of this study, where the frequencies dependence on the small angular variations of BH$_4^-$ are taken into account, the F matrix will be considered constant. In fact, as long as no bond length changes are considered, this approximation is reasonable. In the second part of this work, where the effect on the vibrational frequencies of the B–H bond length variation is analyzed, the F matrix cannot be considered constant anymore. However, at this stage, only the stretch–stretch part is changed, and the relation between the
stretch–stretch force constant elements and the bond length will be discussed.

### RESULTS AND DISCUSSION

#### Small Angular Variations

In this section the effect of the lowering of the BH$_4^-$ symmetry on its vibrational spectrum is analyzed. In particular the symmetry was lowered from $T_d$ to $D_{2d}$, $C_{3v}$, and $C_{2v}$ through small angular variations, as shown in eqs 19, 20 and 21, respectively; the nomenclature of the angles is given according to Table 1.

\[
\alpha = \alpha_{12} = \alpha_{34} \quad \text{and} \quad \alpha_{13} = \alpha_{14} = \alpha_{23} = \alpha_{24}
\]

\[
\alpha_{12} = \alpha_{13} = \alpha_{14} = \alpha_{23} = \alpha_{24}
\]

\[
\alpha_{13} = \alpha_{14} = \alpha_{23} = \alpha_{24} = 109.471
\]

Group theory predicts the observation of splitting of degenerate vibrational modes with decreasing symmetry. Correlation table of the $T_d$ group (see Table 2) indicates the irreducible representations obtained in subgroups of the $T_d$ group.

The GF method allows to quantify the extent of the splitting as a function of the angular deformations according to the eqs 19, 20, and 21. Considering the triply degenerate deformation mode $\nu_4$, it appears that a trigonal deformation leading to $C_{3v}$ results in a huge splitting compared to the one obtained in the deformation leading to $D_{2d}$. This behavior is shown in Figure 2.

In the high pressure experiments on RbBH$_4$ it was noted the formation of a tetragonal phase above 3 GPa; in this phase the site symmetry of the BH$_4^-$ ion is $D_{2d}$. At 4.8 GPa, the Raman spectra show a splitting of 10 cm$^{-1}$ of the $\nu_4$ bands. According to Figure 2, this splitting corresponds to an angular distortion of ca. 2°.

NaBH$_4$ becomes tetragonal at low temperatures. The Raman spectrum at 80 K in Figure 3 shows a splitting of only 5 cm$^{-1}$, corresponding to only 1° deformation.

In the high temperature phase of LiBH$_4$ ($P6_3mc$), the BH$_4^-$ group is located on a site with $C_{3v}$ symmetry. The experimental IR spectrum, shown in Figure 4, reveals a splitting...
of ca. 110 cm$^{-1}$ of the $\nu_4$ mode, corresponding to an estimated angular deformation of 3.7° according to Figure 2. Neutron diffraction experiments\textsuperscript{20} on LiBD$_4$ indicated a distortion of 3°, but the very large thermal ellipsoids for the hydrogen (deuterium) atoms in the crystal makes the experimental value not very accurate.

Bond Length Variation. Once the bond length dependence of the vibrational frequencies is considered, the $F$ matrix cannot be kept constant anymore and its dependence on the B–H distances should be taken into account.\textsuperscript{17,18} It has been shown previously\textsuperscript{21,22} that it is possible to apply Badger’s rule\textsuperscript{17,18} to correlate the B–D stretching frequencies with the experimental B–D bond lengths obtained from neutron diffraction for the cubic alkali borohydrides.

Using the experimental vibrational frequencies and bond lengths for the cubic alkali borohydrides\textsuperscript{21,22} the elements of the stretch–stretch block of the $F$ matrix were adjusted to reproduce the experimental values of the stretching frequencies. The results, collected in Table 3, show that the out-of-diagonal elements remain constant, $F_{ij} = 0.006$ electron mass/(atomic unit of time)$^2$, while the diagonal force constants appear to change linearly with the bond length, following eq 22:

$$F_{ii} = 0.46542 - 0.12351 \cdot R_{ii} \leq 4$$  \hspace{1cm} (22)

The GF calculated bending modes ($\nu_2$ and $\nu_4$) were compared with the ones calculated by using the unmodified Gaussian force matrix, in order to quantify the dependence of the bending modes from the stretch–stretch part of the $F$ matrix. The two sets of values were found to be almost identical, and this means that the different blocks of the matrices are practically independent. The GF calculated bending modes were also compared with the experimental data (see Table 4). Table 4 shows that, for all the systems, the GF calculated bending modes are overestimated by about the same amount.

This modified $F$ matrix was applied to the study of BH$_4^-$ diluted in different alkali halides (MX: BH$_4^-$ with M = Na, K, Rb, Cs and X = Cl, Br, I). Figure S1 of the Supporting Information shows the stretching and bending IR frequencies plotted vs the cubic lattice parameter a. The scatter of the data suggests that the tetrahedral BH$_4^-$ ions experience different local (chemical) pressures due to the different ionic sizes. This local pressure translates then into the B–H bond length change. Using the experimentally observed frequencies,\textsuperscript{24–27} the corresponding bond length were estimated in the following way: the value of the bond length (in eq 22) was varied until the GF calculated frequency matched the experimental frequency of the $\nu_3$ stretching mode. The results are summarized in Figure 5.

Figure 6 compares the calculated and observed $\nu_4$ deformation frequencies for different B–H bond lengths. For most of the data, there is a systematic shift of about 40 cm$^{-1}$, as already noted above (see Table 4).

However, the data points for BH$_4^-$ diluted in cesium halides do not follow this trend. These host crystals have simple cubic (sc) or body centered cubic (bcc) structures, in contrast to all the others which have face centered cubic structures (fcc). It is interesting to note that these three data points are also aligned. In the fcc structure, the BH$_4^-$ ion is surrounded by an

| Table 3. Diagonal ($F_{ii}$ $i \leq 4$) and Out-of-Diagonal ($F_{ij}$ $i,j \leq 4$) Force Constant Values for MBH$_4$ (M = Na, K, Rb, Cs) Series$^a$ |
|----------------|----------------|----------------|----------------|----------------|
| compound       | $F_{ii}$       | $F_{ij}$       | B–H length     | GF frequencies | exp frequencies |
| NaBH$_4$       | 0.192          | 0.006          | 1.178(2)        | 2341 ($\nu_3$) | 2340 ($\nu_3$) |
| KBH$_4$        | 0.187          | 0.006          | 1.196(3)        | 2315 ($\nu_3$) | 2312 ($\nu_3$) |
| RbBH$_4$       | 0.184          | 0.006          | 1.206(2)        | 2299 ($\nu_3$) | 2298 ($\nu_3$) |
| CsBH$_4$       | 0.181          | 0.006          | 1.217(3)        | 2285 ($\nu_3$) | 2287 ($\nu_3$) |
|                |                |                |                | 2255 ($\nu_3$) | 2255 ($\nu_3$) |

$^a$The values are expressed in internal units (hartrees–bohrs–radians). The experimental B–D distance (Å)\textsuperscript{21,22} and the experimental\textsuperscript{21–23} and GF calculated frequencies (cm$^{-1}$) are also shown.

Table 4. GF Calculated and Experimental\textsuperscript{21–23} Bending Modes ($\nu_2$ and $\nu_4$) and Difference between Calculated and Experimental Modes ($\Delta \nu_i = \nu_i^{GF} - \nu_i^{exp}$)$^a$ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>compound</td>
<td>$\nu_2$</td>
<td>$\nu_4$</td>
<td></td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>1274</td>
<td>1312</td>
<td></td>
</tr>
<tr>
<td>KBH$_4$</td>
<td>1246</td>
<td>1285</td>
<td></td>
</tr>
<tr>
<td>CsBH$_4$</td>
<td>1220</td>
<td>1263</td>
<td></td>
</tr>
<tr>
<td>Me$_4$N$_4$BH$_4$ expt</td>
<td>1289</td>
<td>1332</td>
<td></td>
</tr>
<tr>
<td>Me$_4$N$_4$BH$_4$ calcd</td>
<td>1312</td>
<td>1356</td>
<td></td>
</tr>
</tbody>
</table>

$^a$All the values are expressed in cm$^{-1}$.

The Journal of Physical Chemistry C
octahedron of six cations, while in the sc and bcc structure, it is surrounded by a cube of eight cations. The different behavior in Figure 6 suggests that one has also to consider the cation coordination which influences the values of the bending frequencies. These results can also be applied to high pressure studies of the alkali borohydrides in their cubic phases. The slope of Figure 5 indicates that the bond length changes by 0.01 Å for a frequency shift of 15 cm\(^{-1}\) for \(\nu_3\) and 13 cm\(^{-1}\) for the Raman active \(\nu_1\). In the case of NaBH\(_4\)^−, a pressure shift of ca. 25 cm\(^{-1}\)/GPa was observed in the \(Fm\_3\_m\) phase up to 2 GPa, corresponding to an estimated shortening of the B−H bond of about 0.02 Å.

## CONCLUSIONS

We have applied the GF method to calculate the amplitude of angular deformations observed for alkali borohydrides and compared the results with observed experimental spectra. The force field for this calculation was first obtained from DFT calculations for an individual ion. The theoretical level of the calculations does not influence significantly the magnitudes of the splittings upon angular deformations. Our observations also show that the bending mode frequencies are influenced by the coordination of cations around the BH\(_4^−\) ion. This aspect requires further investigations.

Using the published crystal structure data for MBH\(_4\) (M = Na, K, Rb, Cs) and the vibrational spectra of these compounds, we found that an empirical linear relation describes the change in the diagonal B−H stretching force constant with change of the bond length. The application of this relation to a set of experimental data for borohydrides in cubic crystals shows that the B−H bond length varies by more than 0.1 Å in the series of compounds studied. Pressure dependent results for NaNBH\(_4\) are also discussed. It is important to stress that for the two parts of this study, we have either kept the B−H bond length fixed (for the angular deformations) or constrained the geometry to tetrahedral symmetry. Deformations combining both bond length changes and angular deformations will require further investigations to identify the dominating contributions in the F matrix. The approach illustrated in the present work is general and can be applied to other molecules. An interesting study in the field of boron hydrogen compounds could by the study of different deformations of icosahedron B\(_{12}\)H\(_{12}\). (11) Scilab Enterprises

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b06045.

Detailed mathematical description for the tetrahedral molecule, as well as the results from the coupled-cluster calculations, and the plot for BH\(_4^−\) in cubic crystals of the stretching and bending IR frequencies as functions of the lattice parameter (PDF)

## AUTHOR INFORMATION

### Corresponding Author
*(V.D.) E-mail: Vincenza.Danna@ens-lyon.fr.

### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was supported by the Swiss national Science Foundation.

## REFERENCES


