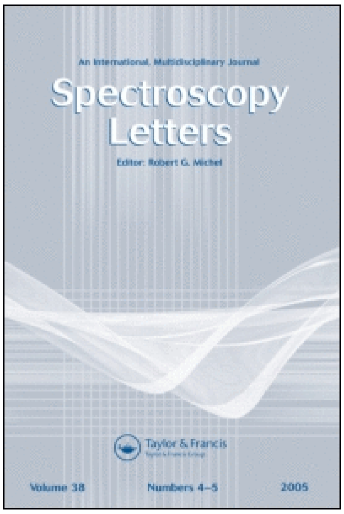

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Quantum Chemical Calculations and Vibrational Spectra of the Hydroxytrifluoroborate Anion

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Quantum Chemical Calculations and Vibrational Spectra of the Hydroxytrifluoroborate Anion

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ABSTRACT

Quantum chemical ab initio calculations at the Möller–Plesset 2 level of theory were performed on the hydroxytrifluoroborate anion, BF_3OH^-, with the aim to assign the infrared and Raman spectra of $K[BF_3OH]$. The frequencies calculated for the normal species, $^{11}BF_3OH^-$, were compared with experimental values. The force constants computed with the 6-31++G(d,p) basis set were employed to evaluate the frequencies of the isotopomers, $^{10}BF_3OH^-$, $^{10}BF_3OD^-$ and $^{11}BF_3OD^-$. The result was used to identify the $^{10}B/^{11}B$ isotope-shifted bands due to the co-presence of the two boron isotopes with natural abundance. Prediction of the

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fundamental vibrations of the deuterium-substituted analogues was performed to classify the hydroxyl group modes and the BF_3O skeleton modes.

Key Words: Hydroxytrifluoroborate anion; MP2 frequencies; Vibrational isotopic effect.

INTRODUCTION

The use of isotopes is a familiar technique in vibrational spectroscopy.[1] Within the Born-Oppenheimer approximation, this is based on the invariance of the potential function under isotope substitutions. In addition to the usual applications, such as simple identification of bands, support for band assignment and force constant refinement, the technique is occasionally purposed for the estimation of unknown experimental data of isotopomers. The application may become more useful when it is appropriately combined with computational tools such as normal coordinate analysis and quantum chemical calculations.

Of the stable isotopes, boron is called to our particular attention because of its natural abundances (^{10}B 19.6 %, ^{11}B 80.4 %). A good difference in atomic mass between the two boron isotopes lets us expect simultaneous observation of the isotope-dependent bands in the same spectra for certain of the fundamentals. For polycrystalline samples, however, the $^{10}B/^{11}B$ isotopic doublets of the bands are not so clearly defined, even for the seemingly simple cases of the tetrafluoroborates.[2–5] That is, the infrared intense absorption (ν_3) in the $1100 cm^{-1}$ region is complicated by broadening of the band caused by site symmetry splitting and correlation field splitting. In addition, it is necessary to consider the presence of the combination bands ($2\nu_4$) in this frequency region. As to the ν_1, ν_2 and ν_4 fundamentals expected in the region below $800 cm^{-1}$, the isotopic separations of the bands are generally too small to be detected as distinct doublet structures in the observed spectra.

The BF_3OH^- anion is isoelectronic to the BF_4^- anion, and has a distorted tetrahedron form. Distortion is presumably more obvious in the BF_3OH^- ion than in the BF_4^- site in crystals. The $^{10}B/^{11}B$ doublets may be easily observable for some of the fundamental bands of the hydroxytrifluoroborate anion. However, only limited studies have been reported so far about vibrational analysis of the BF_3OH^- anion.[6–8] In this article, the internal vibrations of potassium hydroxytrifluoroborate, $K[BF_3OH]$, were investigated with the aid of quantum chemical ab initio calculations to interpret the observed bands in the infrared and Raman spectra. Some spectral features were explained in terms of the isotopic band shifts between $^{10}BF_3OH^-$ and $^{11}BF_3OH^-$.

EXPERIMENTAL

$K[BF_3OH]$ was prepared and treated in accordance with the method described in the literature.[9] The infrared transmission spectra of polycrystalline samples, as Nujol mulls between two KBr plates, were recorded in the 4000–400 cm^{-1} region using a Perkin–Elmer 1600 Fourier transform infrared spectrometer. The Raman spectra of powder samples were measured in the 4000–200 cm^{-1} region using a Jobin-Yvon HG-2S Raman spectrometer, equipped with the 514.5 nm radiation of an argon ion laser for excitation. The infrared (from 2000 to 400 cm^{-1}) and Raman (from 800 to 200 cm^{-1}) spectra are shown in Figures 1 and 2, respectively. The observed frequencies are given in Table 1 with their tentative assignment.

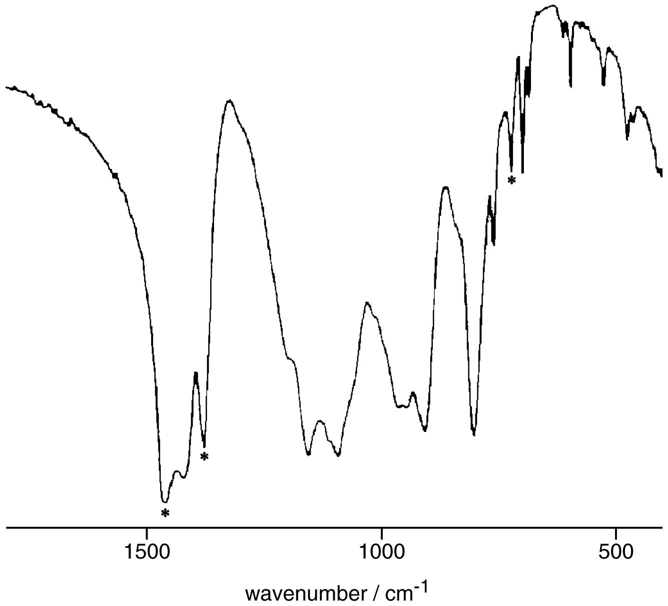

Figure 1. Infrared spectrum in the 2000–400 cm^{-1} region of $K[BF_3OH]$. * Nujol bands.

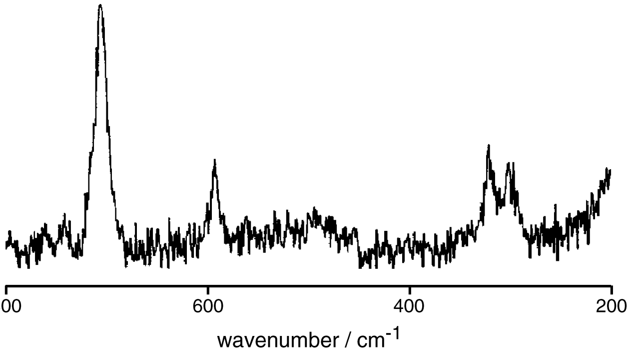

Figure 2. Raman spectrum in the 800–200cm^{-1} region of K[BF_3OH].

CALCULATIONS

Ab initio calculations were performed at the MP2 level of theory using the Gaussian 98 program[10] with the standard Pople basis sets and the valence only basis sets with electron core potentials. In all calculations, the fully optimized structures have a staggered form of C_s symmetry (Figure 3). The experimental geometry of the BF_3OH^- anion is unknown except for the X-ray diffraction structural analysis of Na[BF_3OH] in which the hydroxyl group is treated as an isoelectronic fluorine atom.[11] At the optimized geometry, the Hessian matrix with respect to Cartesian coordinates was analytically computed and then vibrational analysis was performed on the normal isotopomer, $^{11}BF_3OH^-$, for a comparison of the theoretical frequencies and the experimental frequencies. The results are summarized in Table 2. On the whole, the calculated frequencies are well distributed over a wide range of frequency and a tendency in frequency distribution is, comparatively, similar between the basis sets. This means that the calculated frequencies do not change so sensitively, at least within the MP2 level of theory, regardless of the character of the basis set. The 6-31++G(d,p) frequency calculations were extended to the isotopomers, $^{10}BF_3OH^-$, $^{10}BF_3OD^-$ and $^{11}BF_3OD^-$, with the intention to predict the isotopic effects on the fundamental vibrations (Table 3).

RESULTS AND DISCUSSION

Absence of symmetry elements in the BF_3OH^- anion, other than one mirror plane formed by the OH group and the opposite BF bond, permits all

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Table 1. Observed frequencies (cm^{-1}) and assignment of $K[BF_3OH]$.

Infrared	Raman	Assignment
3698 m		νOH (a′)
1423 m		908+528
1199 w		ν_{3a} (a′) − ^{10}B
1158 s		ν_{3a} (a′) − ^{11}B
1113 w		803+320
1095 s		ν_{3b} (a′) − ^{11}B
1015 w		696+320
964 w		2 × 478
948 w		ν_{3c} (a″) − ^{10}B
908 s		ν_{3c} (a″) − ^{11}B
803 s		δOH (a′)
759 w		465+301
696 m	702 s	ν_1 (a′)
683 w		803 − 120(?)
612 w		320+301
596 m	591 m	2 × 301
528 w		ν_{4a} (a′)
478 w		ν_{4b} (a′)
465 w		ν_{4c} (a″)
	320 m	ν_{2b} (a″)
	301 m	ν_{2a} (a′)
–	–	τOH (a″)

12 vibrational modes to be active optically in both the infrared and Raman spectroscopy, $\Gamma = 8a'(IR,R) + 4a''(IR,R)$. Three of those are the hydroxyl group vibrations; OH stretching (νOH), BOH bending (δOH) and torsion about the BO bond (τOH), and other nine modes are the skeletal vibrations of the BF_3O group.

In the earlier infrared investigations of $Na[BF_4]$, the presence of BF_3OH^- species, as a substitution impurity of BF_4^- by traces of water, was revealed by identification of the νOH band.[7,8] The νOH band of BF_3OH^- at $3641\,cm^{-1}$ is shifted to the $2688\,cm^{-1}$ of BF_3OD^- when D_2O is employed instead of H_2O. A variety of spectroscopic measurements under different experimental conditions support this assignment. There is no experimental data relative to the δOH and τOH vibrations. The MP2 frequencies in Table 3 show that the bands computed above $3000\,cm^{-1}$ and below $200\,cm^{-1}$ of BF_3OH^- are characteristically shifted on deuterium substitution. The frequency ratios of about 1.4 are for the H/D isotopic

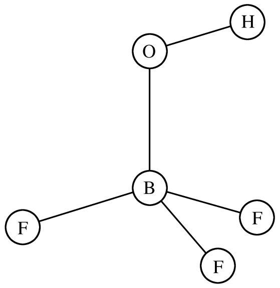

Figure 3. Staggered form of the BF_3OH^- anion optimized by ab initio calculations at the MP2 level of theory.

effect compared to pure OH vibrations. The frequencies are of the νOH and τOH modes, respectively. Accordingly, the infrared band at $3698\,cm^{-1}$ of $K[BF_3OH]$ is straightforwardly assigned to the νOH mode. The torsion mode below $200\,cm^{-1}$ is out of our experimental measurements. The computed third H/D-sensitive band in the $900\,cm^{-1}$ region gives a low-frequency shift of more than $150\,cm^{-1}$ by deuterium substitution and is surely relative to the bending mode of the hydroxyl group. However, the frequency ratio of about 1.2 is significantly less than the value of about 1.4 expected for the pure δOH mode. The value suggests that the contribution

Table 2. MP2 frequencies (cm^{-1}) of $^{11}BF_3OH^-$.

a′ symmetry species	νOH	ν_{3a}	ν_{3b}	βOH	ν_1	ν_{4a}	ν_{4b}	ν_{2a}
Exp.	3698	1158	1095	803	696	528	478	301
6-31+G(d)	3812	1190	1090	929	735	475	509	343
6-31++G(d,p)	3933	1182	1087	928	736	477	509	343
6-311++G(3df,2p)	3942	1180	1080	929	748	485	518	348
aug-cc-pVTZ	3904	1182	1078	935	749	485	517	347

a″ symmetry species	ν_{3c}	ν_{4c}	ν_{2b}	τOH
Exp.	908	465	320	–
6-31+G(d)	989	504	370	137
6-31++G(d,p)	990	504	369	141
6-311++G(3df,2p)	1000	509	368	152
aug-cc-pVTZ	1010	507	364	129

Table 3. MP2/6-31++G(d,p) frequencies (cm^{-1}) of hydroxytrifluoroborate isotopomers.

$^{10}BF_3OH^-$	$^{11}BF_3OH^-$	$^{10}BF_3OD^-$	$^{11}BF_3OD^-$
3933	3933	2861	2861
1216	1182	1167	1124
1125	1087	1113	1074
1030	990	1029	990
941	928	776	774
736	736	720	720
511	509	508	506
505	504	505	504
478	477	456	454
369	369	359	359
343	343	335	335
141	141	105	105

of one or more skeletal vibrations is also required to explain the isotopic effects on the computed frequencies. The shift of about $10 cm^{-1}$ is theoretically anticipated for this fundamental band upon $^{10}B/^{11}B$ substitution. Assignment in the δOH region of the infrared spectra will be made together with the skeletal asymmetric stretching modes.

The skeletal vibrations of the BF_3OH^- anion are analyzed to conform to those of the isoelectronic BF_4^- anion.[4,5] The structure of the reduced representation of the 9 normal modes of the BF_4^- ion is $\Gamma(T_d)=1a_1(\nu_1;$ R$)+1e(\nu_2;$ R$)+2t_2(\nu_3$ and $\nu_4;$ IR,R). By some group theoretical requirements and from a difference in the expected frequency regions, it seems to be reasonable, as a first approximation, that the bond stretching vibrations (ν_1 and ν_3) are dealt with separately from the skeletal deformations (ν_2 and ν_4). In crystals, the gas-phase fundamental vibrations can be split by the effect of crystal symmetry.

The totally symmetric stretching mode (ν_1) of the BF_4^- anion found at about $780 cm^{-1}$, which is selectively active in Raman spectroscopy to T_d symmetry, comes to be observed in infrared spectroscopy as presumed by a factor group analysis. One of the skeletal stretching vibrations of BF_3OH^- may be characterized also as the ν_1 mode that is involved simultaneously in phase movements of the four bonds connected to the central boron atom. This mode does not cause effective displacement of the boron atom and the band position is scarcely affected by $^{10}B/^{11}B$ substitution. The calculated frequency in the $700 cm^{-1}$ region is actually invariant between the $^{10}B/^{11}B$ species and shifts moderately, about $15 cm^{-1}$, upon deuterium substitution.

Brooker reported that the Raman band of BF_3OH^- at $773\,cm^{-1}$ is shifted to $748\,cm^{-1}$ in BF_3OD^-, and assigned those as the BO stretching vibration.[8] In the present investigation, it is confirmed that the Raman band of K[BF_3OH] at $702\,cm^{-1}$ is also observable in the infrared spectra at $696\,cm^{-1}$. Thus, observation in both the Raman and infrared spectra supports the assignment of the band at about $700\,cm^{-1}$ to the ν_1 mode.

As regards the asymmetric stretching vibrations (ν_3) of the BF_4^- anion, the characteristic infrared absorption in the $1100\,cm^{-1}$ region obviously consists of many components. The principal components are assigned to the ν_3 modes, which split in accordance with the site symmetry of the $^{11}BF_4^-$ ion. Some of the weak components coincide with the ν_3 bands of ^{10}B enriched samples. The respective ν_3 bands can split further under the correlation field formed by equivalent anions. In addition to the multiple band structure due to crystal symmetry, binary combinations of the ν_4 modes are also expected in the same frequency region. From the spectra, the $^{10}B/^{11}B$ band separations are about $40\,cm^{-1}$ for the ν_3 modes, while the isotopic effects on the $2\nu_4$ bands are estimated within some wavenumbers.

Although the crystal structure of potassium hydroxytrifluoroborate is not yet known, it is unquestionable that the BF_3OH^- ion is not a perfect tetrahedron and the degenerated modes of T_d symmetry can split it into the components. Nevertheless, it is generally said that the ab initio frequencies at the MP2 level of theory are possibly slightly overestimated with the harmonic approximation. The bands predicted in the $1300–800\,cm^{-1}$ region are good candidates for the ν_3 modes as well as the δOH bending mode. The vibrations require movement of the boron atom and, consequently, an appropriate $^{10}B/^{11}B$ isotopic effect is desirable on the fundamentals. Quantum chemical calculations indicate that there are four well-separated frequencies in the $1300–800\,cm^{-1}$ region for each isotopomer of the hydroxytrifluoroborate anion. The lowest band in the $900\,cm^{-1}$ region was already mentioned as the δOH mode, which is partially mixed with the skeletal modes. The MP2 frequencies in Table 3 point out that three bands at about 1200, 1100 and $1000\,cm^{-1}$ show $^{10}B/^{11}B$ band shifts of about $40\,cm^{-1}$. With respect to H/D substitution, the effect causes shifts of about 60 and $15\,cm^{-1}$, respectively, on the fundamentals at about 1200 and $1100\,cm^{-1}$, whereas the band at about $1000\,cm^{-1}$ is almost not influenced by the substitution. The results mean that the two high-frequency vibrations at about 1200 and $1100\,cm^{-1}$ are the ν_3 modes which belong to a′ species and are slightly mixed with the δOH bending with some difference in extent. Thus, the mode mixing between the a′ species vibrations is confirmed by both sides, that is, the ν_3 bands and the δOH band. Meanwhile, the third vibration at about $1000\,cm^{-1}$ is the ν_3 mode of an a'' species and the coupling with the δOH bending is theoretically prohibited.

Spectroscopic measurements of K[BF_3OH] show that there are no confirmed Raman bands above 800 cm^{-1}. On the other hand, the infrared spectra in the 1300–800 cm^{-1} region are rich in strong absorption bands centered at 1158, 1095, 908 and 803 cm^{-1}. In spite of the significant computational overestimation of about 100 cm^{-1} found on the last two frequencies, assignment of these bands as the fundamentals of the $^{11}BF_3OH^-$ anion appears to be unchallenged. The bands at 1158 and 908 cm^{-1} are accompanied by weak bands at the high frequency side at 1199 and 948 cm^{-1}. The high frequency displacements of about 40 cm^{-1} from the main components are favorable to the $^{10}B/^{11}B$ isotopic effect on the ν_3 modes and the side bands are attributed to the ν_3 modes of the $^{10}BF_3OH^-$ anion. The band at 1095 cm^{-1} is also accompanied by a weak band at 1113 cm^{-1}, but the separation of 18 cm^{-1} is half of the expected 40 cm^{-1} for the ν_3 mode and the difference impedes assignment of the 1113 cm^{-1} band to the remaining ν_3 mode of the $^{10}BF_3OH^-$ ion. The third ν_3 band is expected at about 1135 cm^{-1}, from the isotopic effect, and is probably merged by the strong absorption centered at 1158 cm^{-1}. The single infrared band at 803 cm^{-1}, which possesses a shoulder with an indeterminate peak position, is assigned as the δOH mode of the ordinary $^{11}BF_3OH^-$ anion. The δOH band of the $^{10}BF_3OH^-$ anion may correspond to shoulder on the high frequency side.

According to group theory applied to the point group T_d, the ν_2 skeletal bending modes of e species of the BF_4^- anion are expected only in the Raman spectra, whereas the ν_4 modes of t_2 species are expected theoretically in both the infrared and Raman spectra. The polycrystalline spectra of the tetrafluoroborates indicate that the former is in the 350 cm^{-1} region while the latter is in the 530 cm^{-1} region.[4,5] Hence, two Raman medium bands at 320 and 301 cm^{-1} of K[BF_3OH] are assigned to the ν_2 modes, respectively, of a″ and a′ species based on the MP2 calculations. The band separation of 19 cm^{-1} measured between the a′ and a″ fundamentals is comparable with the computed 27 cm^{-1}. With respect to the triple ν_4 modes, two MP2 frequencies of a′ and a″ species are accidentally degenerated in the 500 cm^{-1} region and the other ν_4 band of a′ species at about 480 cm^{-1} can be characterized as the symmetric bending of the BF_3O group about the B-O axis. On the other hand, there are four observed bands in the 600-450 cm^{-1} region. The medium intensity band at about 600 cm^{-1}, observed in both the Raman and infrared spectra, is inadequate for the ν_4 fundamental because of its too high band position as compared with the computed frequencies. The paired weak infrared bands at 478 and 465 cm^{-1}, which are not found in the Raman spectra, are assigned to the almost degenerated fundamentals. The symmetric skeletal bending mode is attributed to the 528 cm^{-1} infrared band. It is also noted that the frequencies attributed as the ν_4 fundamentals cannot be built as overtones or combinations of the lower ν_2 modes.

The bands observed and not assigned to the fundamentals of $^{10}BF_3OH^-$ or $^{11}BF_3OH^-$ are analyzed as combinations. Those are $1423=908+528$, $1113=803+320$, $964=2\times478$, $759=465+301$, $612=320+301$ and $596=2\times301$. The band at 683 cm^{-1} can not be constructed simply adding the fundamental frequencies, but it may be possible to make a difference between two internal fundamentals as $1158-465=693$ or $803-120(?)=683$. The estimated frequency of 120 cm^{-1} for the second case is very close to the fundamental frequency computed for the τOH torsion mode.

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