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Interplay of experiment and theory: high resolution infrared spectrum and accurate equilibrium structure of $\text{BF}_2\text{OH}^\ddagger$

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The high-resolution Fourier transform infrared (FTIR) spectrum of $^{11}\text{BF}_2\text{OH}$ (difluoroboric acid) is analyzed taking into account numerous interactions. The ν_1 , ν_2 and ν_3 infrared bands are analyzed for the first time, whereas the parameters of the 6^1 , 7^1 , 8^1 and 9^1 states and for the 4^1 and 9^2 interacting states are redetermined. These results are used to check the quality of the *ab initio* force field. It is found that the *ab initio* rovibrational corrections are more accurate than the experimental ones. An earlier attempt to determine a semiexperimental structure did not allow us to obtain an accurate equilibrium structure. The reasons of this failure are investigated. This failure was mainly due to the lack of useful experimental information. Indeed, there is no isotopic substitution available for the fluorine atoms, and the boron atom is extremely close to the center of mass. Furthermore, the available isotopic substitutions ($\text{H} \rightarrow \text{D}$ and $^{16}\text{O} \rightarrow ^{18}\text{O}$) induce a large rotation of the principal axis system which amplifies the errors. However, the mixed estimation method has allowed us to determine a complete and reliable equilibrium structure. Thanks to this method, it is possible to determine an accurate structure, even in extremely difficult cases. An extensive analysis of the quality of structure calculations at the CCSD(T) level is also performed using basis sets up to five ζ quality. It was found that, at the convergence limit, the effects of the diffuse functions are practically disappearing, whereas the core–core and core–valence electron correlation effects are quite important for the bond lengths.

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1. Introduction

The spectra and structure of difluorohydroxyborane molecule or difluoroboric acid, BF_2OH , were studied several times by experimental and theoretical methods. Nevertheless, there are still several problems that could not be solved until now. The molecule was first detected by mass spectrometry.¹ The microwave spectrum of this planar asymmetric rotor was measured several times.^{2–5} The matrix infrared (IR) spectra of eight isotopologues were first observed by Jacox *et al.*⁶ Some of these data for the ^{11}B isotopic species of BF_2OH are also summarized in Table 1, which otherwise quotes the available high resolution infrared data. The first high resolution gas phase IR spectrum of BF_2OH was observed by Collet *et al.*⁷ using a Fourier transform

spectrometer, and this study led to the first investigation of the ν_8 and ν_9 fundamental bands of ^{11}B (for the $^{11}\text{BF}_2\text{OH}$ and $^{10}\text{BF}_2\text{OH}$ isotopic species we will use henceforth in the text the abbreviated notation ^{11}B and ^{10}B , respectively). Subsequently, the high-resolution infrared spectrum was recorded by Fourier transform spectroscopy in the range 400–4000 cm^{-1} .⁸ At that time no significant resonances were observed during the investigation of the ν_5 , ν_8 , ν_9 and $\nu_8 + \nu_9$ bands. On the other hand the ν_7 band was found to be affected by a C-type Coriolis resonance coupling together the 7^1 energy levels with those from the dark 6^1 state. Finally, the ν_4 and $2\nu_9$ bands,⁹ which correspond to the OH in-plane bending mode and to the first overtone of ν_9 (OH torsion relative to the F_2BO moiety), respectively, are strongly perturbed. Indeed, the energy levels of the 9^2 state are involved in B-type Coriolis resonances with those of the 6^19^1 dark state. Moreover, the 4^1 levels are perturbed by B-type Coriolis resonances with 7^19^1 levels and by C-type Coriolis and anharmonic resonances with the 6^17^1 levels. In addition to these rather “classical” perturbations, large amplitude effects were evidenced during the analysis of the $2\nu_9$ and ν_4 bands⁸ and of the $3\nu_9 - \nu_9$ hot band.¹⁰ To give an order of magnitude, for low K_a values, tunnelling splittings of about 0.0051, 0.0038 and 0.031 cm^{-1} were observed for the energy levels of the 9^2 , 4^1 and 9^3 states, respectively. There is a slow decrease of these splittings for high K_a values that are difficult to observe in the

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Table 1 Fundamental bands of $^{11}\text{BF}_2\text{OH}$ and interactions (values in cm^{-1} when pertinent)

State ^a	Description	ν (exp.)	$\Delta\omega^b$	Interaction parameter ^b
ν_9, A''	$\delta(\text{BOH})$ o.p.	522.87 ^c	$\omega_9 - \omega_7 = 101$ $\omega_9 - \omega_6 = 72$	$\zeta_{79}^a = 0.33; \zeta_{79}^b = -0.11$ $\zeta_{69}^a = -0.15; \zeta_{69}^b = -0.01$
ν_8, A''	$\delta(\text{F}_2\text{BO})$ o.p.	684.16 ^c	$\omega_6 - \omega_8 = 211$	$\zeta_{68}^a = -0.26; \zeta_{68}^b = 0.16$
ν_7, A'	$\delta(\text{F}_2\text{BO})$ i.p.	446.54 ^c	$\omega_6 - \omega_7 = 30$ $\omega_9 - \omega_7 = 101$	$\zeta_{67}^c = 0.75$ $\zeta_{79}^a = 0.33; \zeta_{79}^b = -0.11$
ν_6, A'	$\nu(\text{F}_2\text{BO})$ i.p.	479.17 ^c	$\omega_9 - \omega_6 = 72$ $\omega_6 - \omega_7 = 30$ $\omega_6 - \omega_8 = 211$	$\zeta_{69}^a = -0.15; \zeta_{69}^b = -0.01$ $\zeta_{67}^c = 0.75$ $\zeta_{68}^a = -0.26; \zeta_{68}^b = 0.16$
ν_5, A'	$\delta(\text{BF}_2)$ i.p.	880.74 ^c	$\omega_5 - 2\omega_7 = 9$ $\omega_5 - \omega_6 - \omega_7 = -21$	$\phi_{577}^c = -0.8$ $\phi_{567}^c = -0.4$
ν_4, A'	$\delta(\text{BOH})$ i.p.	961.49 ^d	$\omega_4 - \omega_7 - \omega_9 = 17$ $\omega_4 - \omega_6 - \omega_7 = 89$ $\omega_4 - 2\omega_9 = -84^f$	${}^{79,4}B_x = -0.167274^e$ $\phi_{467} = 2.2$ $\phi_{499} = 108$
ν_3, A'	$\nu_s(\text{BF})$ i.p.	1419.2126 ^g	$\omega_2 - \omega_3 = 52$	$\zeta_{23}^c = 0.798$
ν_2, A'	$\nu_{as}(\text{BF})$ i.p.	1468.2762 ^g	$\omega_2 - \omega_3 = 52$ $\omega_2 - \omega_4 - \omega_6 = 7$ $\omega_2 - \omega_4 - \omega_7 = 36$	$\zeta_{23}^c = 0.798$ $\phi_{246} = -6$ $\phi_{247} = 2$
ν_1, A'	$\nu(\text{OH})$ i.p.	3714.12 ^g	$2\omega_2 + \omega_5 - \omega_1 = 9$ $2\omega_3 + \omega_4 - \omega_1 = 16$ $2\omega_3 + \omega_5 - \omega_1 = -94$	— — —

^a A' and A'' are the symmetry species in the C_s point group. ^b CCSD(T)_AE/TZ2Pf value, see text; $\Delta\omega$ is the harmonic frequency. ^c Gas phase band centers from ref. 8. ^d Gas phase band centers from ref. 9. ^e Experimental value, this work. ^f Experimental value for $2\nu_9 = 1042.87 \text{ cm}^{-1}$. ^g This work.

infrared region. These large amplitude effects for BF_2OH were confirmed by a careful reinvestigation of the rotational spectrum by millimeterwave spectroscopy.⁵ In this study, torsional splittings were found for most of the rotational transitions within the ground state and could be satisfactorily reproduced using the IAM (internal axis method) formalism. Using this approach, reasonable agreement between the *ab initio* (0.0061 and 0.0043 cm^{-1}) and experimental (0.0038 and 0.0051 cm^{-1}) tunnelling splittings for the 4^1 and 9^2 states could be achieved. These results were later confirmed by another *ab initio* study.¹¹

Ab initio calculations predict the existence of many vibrational-rotational resonances perturbing the rotational structure of most vibrational states of BF_2OH .⁴ These additional resonances which were not accounted for during our previous energy level calculations⁷⁻⁹ will be considered here for the 6^1 , 7^1 , 8^1 and 9^1 states and for the 4^1 and 9^2 interacting states.

The equilibrium geometry and anharmonic force field up to semidiagonal quartic terms have been calculated at the coupled cluster level of theory including a perturbational estimate of the effects of connected triple excitations [CCSD(T)].⁴ The semiexperimental structure (SE) was also determined using a force field of CCSD(T) quality, but the result was not satisfactory. One of the main goals of this paper is to try to explain the reason for this failure and to propose solutions. There are two obvious explanations: there is no isotopic substitution available for the fluorine atom. Furthermore, the boron atom is extremely close to the center of mass; in other words, the substitution $^{11}\text{B} \rightarrow ^{10}\text{B}$ does not bring useful information. In conclusion, there are not enough data (*i.e.* rotational constants) available. There is one more reason: BF_2OH is an oblate molecule and isotopic substitutions may induce large rotations of the principal axis system (PAS) that may amplify the errors.¹² This point will be confirmed here. Finally, it is also possible that the large amplitude motion of the OH group hinders an accurate determination of the semiexperimental structure. This last point will be investigated here.

The semiexperimental (SE) structures of several molecules with a large amplitude motion have already been determined. In the case of molecules with a methyl group (propene,¹³ methyl formate,¹⁴ dimethyl ether,¹⁵ dimethyl sulfide¹⁶), the internal rotation does not seem to affect negatively the accuracy of the SE structure. For molecules with an OH group, the situation is more complicated.¹⁷ It was possible to obtain accurate SE structures for nitrous acid (*syn* and *anti* conformers),^{18,19} formic acid (*syn* and *anti* conformers)²⁰ as well as glycolaldehyde.¹⁷ On the other hand, for proline²¹ and glycidol,¹⁷ the SE rotational constants of the OD species were found to be incompatible with the best structure. Finally, although accurate SE structures could be determined for ethanol (*anti* conformer)¹⁷ and nitric acid,²² there was obviously a problem: the rotation-vibration interaction constants (α -constants) of the lowest fundamental vibration could not be reproduced accurately by the *ab initio* force field. It might lead us to think that it is due to the large amplitude vibration. However, the same problem is encountered in some rigid molecules such as HCOCl ²³ and vinyl fluoride.²⁴ An alternative explanation is that the structure used to calculate the *ab initio* force field is not accurate and might therefore lead to inaccuracies in some α -constants. BF_2OH is a favourable case to check this hypothesis because it is a rather small molecule; furthermore, it is planar.

In the present paper, after a short description of the experimental details, the spectra for the ν_1 , ν_2 and ν_3 bands are analyzed. The energy levels for the 1^1 , 2^1 and 3^1 vibrational states as well as the $\{6^1, 7^1, 8^1, 9^1\}$ and $\{4^1, 7^1, 9^1, 6^1, 7^1, 9^2, 6^1, 9^1\}$ resonating states are computed, and the molecular parameters are subsequently determined. Then, the accuracy of the Born-Oppenheimer *ab initio* structure is confirmed. Next, the quality of the *ab initio* anharmonic force field is evaluated followed by a discussion of the accuracy of the rovibrational corrections. Finally, the difficulties inherent in the determination of the semiexperimental structure are examined, and the SE structure is determined using the method of mixed estimation.



2. Experimental details

The details of the synthesis of the enriched isotopologues ^{10}B (92.4%) and ^{11}B (99%) of BF_2OH and the recording of the high resolution FTIR spectra are given in ref. 8. The resolution (1/maximum optical path difference) was adjusted to $2.4 \times 10^{-3} \text{ cm}^{-1}$, and the precision and wavenumber accuracy are better than 0.5×10^{-3} and better than $1 \times 10^{-3} \text{ cm}^{-1}$.⁸

As usual, water lines²⁵ were observed as impurities in both spectral regions. In addition, the analysis was complicated in the $1430\text{--}1470 \text{ cm}^{-1}$ region by the presence of lines from the strong ν_3 perpendicular band of the $^{11}\text{BF}_3$ impurity centered at 1453.98 cm^{-1} .²⁶

3. Analysis

In the present infrared study it was possible to perform the first high resolution analysis of the ν_2 and ν_3 bands together with the first identification of the ν_1 band of ^{11}B .

During this study, the ground state energy levels were computed using the accurate ground state constants derived in ref. 4 and, as a model, a Watson A-type Hamiltonian written in I^f representation.²⁷ For symmetry reasons, ν_1 , ν_2 and ν_3 are, in principle, hybrid bands with both A- and B-type transitions. Fig. 1 and 2 give overviews of the ν_1 band and of the ν_2 and ν_3 bands, respectively. In fact, the ν_1 and ν_2 are mainly pure A-type bands while both A- and B-type transitions were observed for the ν_3 band. For these three bands the Q branches are rather narrow, while in the P and R branches, lines are grouped into clusters, and each “s” cluster gathers together transitions $[J, K_a, K_c] - [J \pm 1, K_a, K_c \pm 1]$, involving the same value of “s” with

$$s = 2J - K_c \quad (1)$$

For these unresolved doublet transitions,⁸ J is the rotational quantum number and K_a, K_c are pseudo quantum numbers that

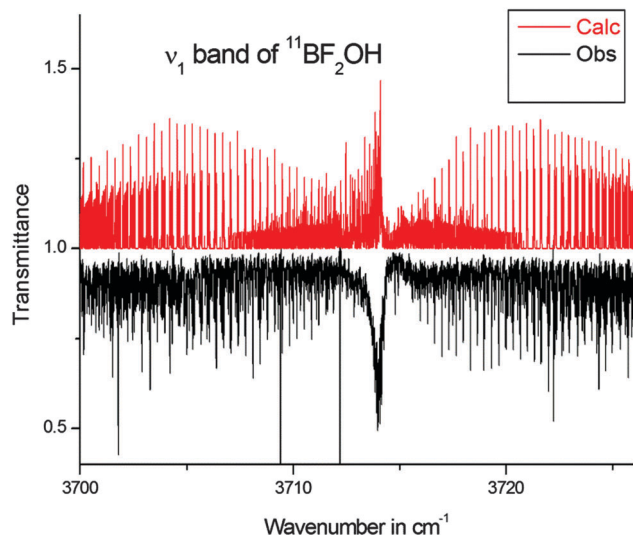


Fig. 1 The A-type ν_1 band of BF_2OH .

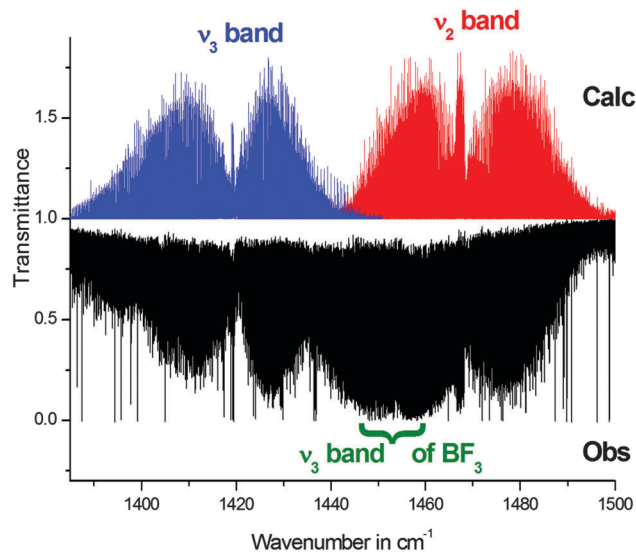


Fig. 2 Overview of the ν_2 and ν_3 bands of BF_2OH . In this spectral region, impurity lines from the ν_3 band of BF_3 are also clearly observable.

correlate with the $K = |k|$ quantum number about the a and c axes in the prolate and oblate symmetric top limits, respectively.

The first identifications were initiated by taking advantage of line regularities from one cluster to another one in the P and R branches. Once a few lines were assigned, the energy levels of the various upper vibrational states were computed by adding to the observed line positions the computed ground state energies. These first sets of energy levels were included in a least squares fit, and a first set of vibrational energies and upper state rotational constants were determined for the 1^1 , 2^1 and 3^1 vibrational states. With these first sets of constants it was possible to make better predictions and hence to assign new lines. The process was repeated until it was no longer possible to perform new assignments.

For the ν_2 band, the assignment is rather complete, because the band is only weakly perturbed. On the other hand, the ν_3 band is highly perturbed, and this is why the analysis concerns only several series involving low K_a values.

For the ν_1 band, the assignments are restricted to the identification of the “s” clusters in the P and R branches (see eqn (1)), with $s \leq 33$, and no detailed and faithful information can be obtained on the rotational structure within each cluster in the $3600\text{--}3800 \text{ cm}^{-1}$ region. This limitation is because the Doppler line width of each individual line ($\sim 0.028 \text{ cm}^{-1}$ at 296 K) in each cluster is already of the order of magnitude of the separation between two adjacent lines belonging to the same cluster. Furthermore, we presume that the ν_1 band is perturbed, and this complicated further the analysis.

4. Energy level calculations

4.1. Theoretical model

Several vibration–rotation resonances were accounted for, depending on the resonating states considered. A brief description of the



Hamiltonian models that we had to use to perform these calculations is given in the Appendix. As in ref. 9 the Euler angle θ , which could not be determined, was set at zero.

4.2. The 1^1 , 2^1 and 3^1 states

For the 2^1 state and 3^1 vibrational states we present two calculations. The first one was done assuming that these states are isolated, while the second one accounts for the C-type Coriolis resonance which couples together the 2^1 and 3^1 energy levels. Among the set of 2^1 and 3^1 measured energy levels, only those which can be considered as “less perturbed” by resonances involving dark states were considered in the least squares fit calculations. The parameters (vibrational energies, rotational constants and C-type interacting parameter) resulting from these computations are quoted together with their associated uncertainties in Table 2. The A rotational constants proved to be non-determinable and were maintained fixed at the value proposed by Breidung *et al.*⁴ Table S1 of the ESI† gathers details of the energy level calculations in terms of standard deviations and statistical analyses. It appeared that these two calculations (coupled and uncoupled) differ only marginally in terms of the quality of the fit. This outcome is expected because the resonances involving 2^1 and 3^1 energy levels with those of unidentified dark states were not considered during these two calculations.

Finally, we performed an energy calculation for the 1^1 state. As input for the least squares fit calculation, we used the “pseudo” 1^1 energy levels obtained from the identification of the “ s ” clusters in the P and R branches (see eqn (1)). Among the resulting parameters generated during this fit (see Table 2) only the vibrational energy ($E_1 = 3714.1142 \text{ cm}^{-1}$) has a physical meaning. Indeed, the A , B and C rotational constants which

have clearly unrealistic values are quoted because these parameters were used to model the ν_1 band presented in Fig. 1.

4.3. The $\{6^1, 7^1, 8^1, 9^1\}$ and $\{4^1, 7^1 9^1, 6^1 7^1, 9^2, 6^1 9^1\}$ resonating states

The experimental energy levels of 7^1 , 8^1 and 9^1 (resp. of those 4^1 , $7^1 9^1$ and 9^2) resulting from the analysis performed in ref. 8 (resp. ref. 9) were introduced in a least squares fit calculation to determine the parameters (band centers, rotational and interacting constants, together with, eventually, torsional constants) for the $\{6^1, 7^1, 8^1, 9^1\}$ (resp. $\{4^1, 7^1 9^1, 6^1 7^1, 9^2, 6^1 9^1\}$) resonating states.

The goal of these new calculations was to account explicitly for the Fermi, or A-type, B-type and C-type Coriolis resonances predicted by the *ab initio* calculations.

The parameters (vibrational energies, rotational constants and interacting parameters) resulting from this computation are quoted together with their associated uncertainties in Tables 3–5.

Let us mention that the 6^1 band center was fixed at 479.17 cm^{-1} which corresponds to the infrared broad Q branch structure observed in the FTIR spectra recorded at Wuppertal.⁸ Also, the zero order term involved in the expansion of the Fermi operator coupling the $4^1 \leftrightarrow 9^2$ interacting states was maintained fixed at the value predicted by the *ab initio* calculation:

$${}^{99,4}F_0 = 27.1 \text{ cm}^{-1} \quad (2)$$

The results of these new energy level calculations are satisfactory (standard deviation of $0.30 \times 10^{-3} \text{ cm}^{-1}$ and $0.82 \times 10^{-3} \text{ cm}^{-1}$, respectively) and do not differ in quality from those achieved during our previous calculations (see details of the statistical analysis of the results in Table 5 in ref. 8 and Table 3 in ref. 9).

Table 2 Hamiltonian constants (in cm^{-1}) for the 1^1 , 2^1 and 3^1 vibrational states of ${}^{11}\text{BF}_2\text{OH}$ assumed isolated and for the $\{2^1, 3^1\}$ interacting vibrational states^a

	E_v	A	B	C	${}_{2,3}C_y^d$
0^b		0.3442527640	0.3368801590	0.1699552140	
1^1	3714.1143(8)	0.3437337(170)	0.3359471(285)	0.16984120(148)	0
2^1	1468.2741(48)	0.3427690(200)	0.3357875(320)	0.17047311(780)	0
3^1	1419.1696(34)	0.343047867 ^c	0.3365527(520)	0.16787843(700)	0
2^1	1468.2733(22)	0.34277878(790)	0.3357541(130)	0.168557(240)	0.3087(190)
3^1	1419.1758(47)	0.343047867 ^c	0.3365758(670)	0.169788(240)	

^a All centrifugal distortion constants are fixed to the ground state values. ^b Fixed to the ground state values. ^c For 3^1 the A rotational constant is maintained at the value predicted by Breidung *et al.*⁴ ^d C-type Coriolis constant.

Table 3 Hamiltonian constants (in cm^{-1}) for the $\{6^1, 7^1, 8^1, 9^1\}$ interacting vibrational states of ${}^{11}\text{BF}_2\text{OH}$

	6^1	7^1	8^1	9^1
E_v	479.17 ^a	446.55171(7)	684.15840(7)	522.86815(5)
A	0.3459420(900)	0.344720533(186)	0.343991965(110)	0.343258360(600)
B	0.335897(141)	0.337393954(636)	0.336966965(240)	0.336529392(380)
C	0.1690340(173)	0.170573446(520)	0.170199092(58)	0.169986115(190)
$\Delta_K \times 10^6$	^b	0.354948(940)	0.361381(230)	0.351405(710)
$\Delta_{JK} \times 10^6$	^b	^b	-0.123463(220)	-0.1049458(280)
$\Delta_J \times 10^6$	^b	0.204124(910)	0.208940(420)	0.2004195(110)
$\Delta_K \times 10^6$	^b	0.19104(370)	0.172065(150)	0.174388(230)
$\Delta_J \times 10^7$	^b	0.96250(540)	^b	0.898740(630)

^a All other centrifugal distortion constants are fixed to the ground state values. ^b Fixed to the infrared observed broad structure (see text in ref. 8).



Table 4 Interaction parameters (in cm^{-1})

ν'	ν''	Interaction	Operator	Parameter ^a
8 ¹	6 ¹	Coriolis	\hat{J}_z	${}^{8,6}A_z$ -0.216284(120)
8 ¹	6 ¹		\hat{J}_x	${}^{8,6}B_x$ 6.3943(460) $\times 10^{-2}$
9 ¹	7 ¹		\hat{J}_z	${}^{9,7}A_z$ 0.226997(780)
9 ¹	7 ¹		\hat{J}_x	${}^{9,7}B_x$ -7.4093(140) $\times 10^{-2}$
6 ¹	7 ¹		\hat{J}_y	${}^{6,7}C_y$ 0.284975(340)
9 ¹	6 ¹		\hat{J}_z	${}^{9,6}A_z$ -0.104092(960)
9 ²	4 ¹	Fermi		${}^{99,4}F_0$ 27.1 ^b
7 ¹ 9 ¹	4 ¹	Coriolis	\hat{J}_x	${}^{79,4}B_x$ -0.16727377(550)
			$\{\hat{J}_z^2, \hat{J}_x\}$	${}^{79,4}B_{xzz}$ 1.05205(130) $\times 10^{-5}$
			$\hat{J}_x \hat{J}^2$	${}^{79,4}B_{xf}$ -5.5892(110) $\times 10^{-6}$
			$(\hat{J}_+^2 + \hat{J}_-^2)$	${}^{79,4}B_{x3}$ -1.5266(180) $\times 10^{-7}$
6 ¹ 9 ¹	9 ²	Coriolis		${}^{69,99}B_{yz}$ 1.67146(130) $\times 10^{-3}$
6 ¹ 7 ¹	4 ¹	Anharmonic	\hat{J}_{xy}^2	${}^{67,4}Anh_{xy}$ 3.96636(240) $\times 10^{-4}$
			$\{\hat{J}_z^2, \hat{J}_{xy}\}$	${}^{67,4}Anh_{xyzz}$ -9.72824(590) $\times 10^{-8}$

^a For definitions, see Appendix. ^b Fixed to the *ab initio* value.

The values achieved during this work for the h^{TORS} (torsional) and h^{BEND} (bending) splitting parameters ($h^{\text{TORS}} = 2.60833(250) \times 10^{-3} \text{ cm}^{-1}$ and $h^{\text{BEND}} = 1.82179(270) \times 10^{-3} \text{ cm}^{-1}$, see Table 5) do not differ significantly from those obtained in ref. 9, when neglecting the Fermi resonance coupling $4^1 \leftrightarrow 9^2$ ($h^{\text{TORS}} = 2.54516(1000) \times 10^{-3} \text{ cm}^{-1}$ and $h^{\text{BEND}} = 1.78523(100) \times 10^{-3} \text{ cm}^{-1}$; see Table 8 in ref. 9). Clearly, the torsional splitting in the 4^1 state is not due to the existence of the weak Fermi resonance coupling the 4^1 and 9^2 states.

The assigned lines are given in Table S2 of the ESI.[†]

5. *Ab initio* equilibrium structure‡

The *ab initio* equilibrium structure has been previously optimized with the coupled cluster method with single and double excitations²⁸ and a perturbative treatment of connected triples,²⁹ CCSD(T), along with the correlation-consistent polarized valence n -tuple- ζ basis sets

‡ In the present study, the CCSD(T) calculations were performed with the MOLPRO program package developed by H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz, P. Celani, G. Knizia, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni and T. Thorsteinsson, MOLPRO, 2009. See also: H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby and M. Schütz, *WIREs Comput. Mol. Sci.*, 2012, 2, 242–253. The MP2 and B2PLYPD calculations were carried out by means of the GAUSSIAN09 program: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, GAUSSIAN09, Rev.C.01, 2010, Wallingford, CT.

(cc-pVnZ with $n = 3, 4$).³⁰ The inner-shell correlation was estimated with the second-order Møller–Plesset perturbation theory, MP2,³¹ and the Martin–Taylor (MT) basis set.³² To account for the electronegative character of the F and O atoms, the augmented cc-pVQZ³³ basis set was used at the MP2 level. To investigate the structural effects of further basis set improvement (cc-pVQZ \rightarrow cc-pV5Z), the cc-pV5Z basis set was employed at the MP2 level. The derived structure is expected to be accurate. However, to estimate its precision, we repeated the optimization using different schemes.

First, the augmented correlation-consistent polarized weighted core–valence n -tuple- ζ , aug-cc-pwCVnZ, basis sets³⁴ with $n = D, T, Q, 5$ were used, and all electrons were correlated (AE); consequently,

$$r_e^{\text{BO}}(\text{I}) = r_e[\text{CCSD(T)}_{\text{AE}}/\text{aug-cc-pwCV5Z}]. \quad (3)$$

The cc-pwCVnZ basis sets were also used without the diffuse functions (aug),

$$r_e^{\text{BO}}(\text{II}) = r_e[\text{CCSD(T)}_{\text{AE}}/\text{cc-pwCV5Z}]. \quad (4)$$

The smaller basis sets, $n = D, T, Q$, allow us to check the rate of convergence. The results are given in Table 6, and the details are given in Table S3 of the ESI.[†] It is interesting to note that the two types of basis sets with and without the aug functions converge towards the same limit.

The r_e^{BO} structure was also estimated in the frozen core, FC, approximation using the cc-pV5Z and aug-cc-pV5Z basis sets and the CCSD(T) method. The core–core and core–valence correlation is missing from this treatment. Therefore, the correlation corrections were estimated as differences between the values from AE and FC results at the CCSD(T) level using the cc-pwCVTZ, cc-pwCVQZ and cc-pwCV5Z basis sets, as well as at the MP2 level with cc-pwCVQZ and MT basis sets (see Table S4 of the ESI.[†]). Consequently, the r_e^{BO} structures could be estimated by the following alternative schemes:

$$r_e^{\text{BO}}(\text{III}) = r_e[\text{CCSD(T)}_{\text{FC}}/\text{aug-cc-pV5Z}] + r_e[\text{CCSD(T)}_{\text{AE}}/\text{cc-pwCV5Z}] - r_e[\text{CCSD(T)}_{\text{FC}}/\text{cc-pwCV5Z}] \quad (5)$$

and

$$r_e^{\text{BO}}(\text{IV}) = r_e[\text{CCSD(T)}_{\text{FC}}/\text{cc-pV5Z}] + r_e[\text{CCSD(T)}_{\text{AE}}/\text{aug-cc-pwCV5Z}] - r_e[\text{CCSD(T)}_{\text{FC}}/\text{cc-pwCV5Z}]. \quad (6)$$

As seen in Table S4 of the ESI,[†] the core correlation correction is practically converged at the CCSD(T)_{AE}/cc-pwCVQZ level. The MP2/cc-pwCVQZ level of theory also gives satisfactory results, the much smaller MT basis set giving results of comparable quality. Another interesting result is that the aug-cc-pVnZ and cc-pVnZ basis sets converge towards the same limit. For the above structures, the accuracy is not limited by the basis set convergence but by the approximate (perturbative) treatment of connected triples and the neglect of higher-order connected excitations in the coupled cluster method.

A further, cheaper scheme was also utilized. The structure was computed with the smaller cc-pwCVTZ basis set and the CCSD(T)_{AE} method, and the effect of further basis set enlargement,



Table 5 Hamiltonian constants for the ($4^1, 7^1 9^1, 6^1 7^1, 9^2, 6^1 9^1$) resonating states of $^{11}\text{BF}_2\text{OH}$ (all constants are in cm^{-1} , and the quoted errors are for one standard deviation)

	9^2	$6^1 9^1$	4^1	$7^1 9^1$	$6^1 7^1$
ϕ^{TORS} (in degree)	1.208 ^a		1.208 ^a		
θ^{TORS} (in degree)	0 ^a		0 ^a		
$h^{\text{TORS}} \times 10^3$	2.60833(250)		1.82179(270)		
E_v	1032.53828(1)	1000.82(1)	971.83087(1)	970.99658(3)	929.139(3)
$h_{xz}^v \times 10^3$	-4.05497(110)	-4.05497 ^b	-1.36327(420)	1.36327 ^c	1.36327 ^c
A	0.34190504(170)	0.3408277(140)	0.34300764(210)	0.34311909(250)	0.3756801(120)
B	0.33889632(170)	0.3378665(170)	0.33816039(210)	0.33807857(260)	0.32184572(520)
C	0.1700720766(21)	0.17037573(980)	0.1697909588(100)	0.1680388324(57)	0.17247533(120)
$\Delta_K \times 10^6$	0.292585(280)	^d	0.537199(460)	0.303302(720)	-4.0435(150)
$\Delta_{JK} \times 10^6$	0.052391(260)	^d	-0.415120(290)	-0.106694(760)	5.0582(100)
$\Delta_J \times 10^6$	0.17240131(160)	-0.00863(150)	0.260944291(770)	0.181817(210)	0.10280(270)
$\delta_K \times 10^6$	0.135086(130)	^d	0.151381(150)	^d	^d
$\delta_J \times 10^7$	0.7359108(170)	^d	1.1828284(230)	1.34300(110)	-5.7426(130)

^a The angles ϕ^{TORS} and θ^{TORS} in degree were maintained at the values determined in ref. 8. ^b Fixed to the 9^2 value. ^c Fixed to the 4^1 value. ^d All other centrifugal distortion constants are fixed to the ground state value.⁴

Table 6 Equilibrium structure of BF_2OH (distances in Å and angles in degree)

	$r_e^{\text{BO}}(\text{I})^a$	$r_e^{\text{BO}}(\text{II})^a$	$r_e^{\text{BO}}(\text{III})^a$	$r_e^{\text{BO}}(\text{IV})^a$	$r_e^{\text{BO}}(\text{V})^a$	$r_e^{\text{SE } b}$				
BF_{syn}^c	1.3231	1.3226	1.3229	1.3229	1.3230	1.3248(12)	1.3238(3)	1.3238(1)	1.3239(2)	
$\text{BF}_{\text{anti}}^c$	1.3131	1.3127	1.3130	1.3130	1.3131	1.3128(11)	1.3138(3)	1.3138(1)	1.3139(2)	
BO	1.3449	1.3446	1.3449	1.3449	1.3453	1.3428(2)	1.3428(4)	1.3428(2)	1.3426(3)	
OH	0.9575	0.9573	0.9573	0.9573	0.9576	0.9583(4)	0.9574(11)	0.9585(4)	0.9581(6)	
$\angle(\text{OBF}_{\text{syn}})$	122.24	122.24	122.24	122.24	122.28	122.23(9)	122.30(2)	122.31(1)	122.31(2)	
$\angle(\text{BOH})$	113.14	113.12	113.11	113.11	112.98	113.12(4)	113.14(7)	113.06(3)	113.09(4)	
$\angle(\text{OBF}_{\text{anti}})$	119.39	119.39	119.39	119.39	119.34	119.54(9)	119.46(2)	119.46(1)	119.47(2)	
$\angle(\text{FBF})$	118.37	118.37	118.37	118.37	118.38	118.23(2)	118.23(3)	118.23(2)	118.22(3)	
κ^d							3480	478	424	402
predicates										
OH							0.9585(20)		0.9585(20)	0.9585(20)
$\text{BF}_{\text{syn}}-\text{BF}_{\text{anti}}$								0.010(1)	0.010(1)	0.010(1)
$\angle(\text{BOH})$							113.14(20)	113.14(20)		113.14(20)

^a For definitions, see eqn (3)–(6). ^b For the definition of the predicates, see text. The best structure is given in the last column. ^c F atom is in synperiplanar or antiperiplanar position with respect to the OH bond. ^d Condition number of the fit.

cc-pwCVTZ \rightarrow cc-pwCVQZ, was estimated at the MP2 level. In other words, the r_e^{BO} parameters are obtained using the following equation:

$$r_e^{\text{BO}}(\text{V}) = r_e[\text{CCSD(T)}_{\text{AE}}/\text{cc-pwCVTZ}] + r_e[\text{MP2(AE)}/\text{cc-pwCVQZ}] - r_e[\text{MP2(AE)}/\text{cc-pwCVTZ}]. \quad (7)$$

The basic assumption of eqn (7) is that the correction due to basis set enlargement, cc-pwCVTZ \rightarrow cc-pwCVQZ, is small and can, therefore, be estimated at the MP2 level. This approximation was investigated in several previous studies by us and was found to be reliable. Here, again it is confirmed that this approximation gives results which are accurate enough.^{35–38}

In conclusion, when the basis set used is large enough, there is no need to use the augmented functions, and the MT basis set seems to be accurate enough to estimate the core correlation. In other words, an accurate structure may be obtained.

6. Semiexperimental structure

6.1. Anharmonic force field

The anharmonic force field has been previously calculated at the CCSD(T)_{AE}/TZ2Pf level of theory.⁴ The theoretical fundamental

wavenumbers of the different isotopologues were found to be in good agreement with their experimental counterparts. Furthermore, the *ab initio* quartic centrifugal distortion constants are also in good agreement with the experimental ones. This agreement is an indication that the *ab initio* force field is likely to be accurate. Generally, it is more difficult to compute an accurate *ab initio* harmonic force field than a cubic one.³⁹ We have tried to improve the *ab initio* harmonic force field by fitting at the best equilibrium structure, $r_e^{\text{BO}}(\text{I})$, the experimental quartic centrifugal distortion constants and the harmonic frequencies derived from the experimental fundamental frequencies and the anharmonicity corrections $\omega_i - \nu_i$. No significant improvement was found. This fact confirms that the *ab initio* harmonic force field is probably indeed accurate.

6.2. Rovibrational corrections‡

There is little difficulty obtaining accurate ground state rotational constants. Therefore, the accuracy of the derived SE structure depends on the accuracy of the rovibrational corrections. They were calculated at the CCSD(T)_{AE}/TZ2Pf level of theory.⁴ As a first check, they were also calculated with the Kohn–Sham density



functional theory (DFT)⁴⁰ using the B2PLYPD double hybrid exchange–correlation functional with long range dispersion correction,⁴¹ along with the 6-311+G(3df,2pd) basis set. The results of this lower-level calculation give a first indication that the rovibrational correction is indeed reliable. Indeed, for the unperturbed state 5¹, the values at the B2PLYPD/6-311+G(3df,2pd) level of theory are (in MHz) $\alpha_5^A = 20.9$, $\alpha_5^B = 19.8$ and $\alpha_5^C = 10.6$. These values are close to the CCSD(T)_AE/TZ2Pf ones; see Table 7.

As a further check, it is tempting to compare the experimental α -constants to the ones computed from the *ab initio* cubic force field. However, even when the rotational constants of all fundamental states have been determined, which is often an extremely difficult task, the experimental α -constants are different from the *ab initio* ones. The main cause is that a vibrational state is rarely isolated and, therefore, the derived rotational constants depend on the interactions that have been taken into account; see Section 4. There are numerous interactions between the fundamental states of ¹¹BF₂OH. As shown in Table 1, there is no isolated state. However, although the harmonic frequencies ω_5 and $2\omega_7$ are almost degenerate, the Fermi interaction $\nu_5/2\nu_7$ seems to be negligible due to the almost vanishing cubic constant $\varphi_{577} = -0.8 \text{ cm}^{-1}$. As a consequence, there is a very good agreement between the experimental and computed α 's for the 5¹ state. There is a very strong *c*-type interaction between the states 6¹ and 7¹. However, it is still possible to determine the rotational constants from the low-*J* transitions neglecting this interaction. The corresponding experimental α^C -constants are in good agreement with the computed ones; the same holds for the states 3¹, 4¹, 5¹, 8¹ and 9¹ for which there is no significant interaction affecting the *C* rotational constant (see Table 7). On the other hand, when the Coriolis interaction is taken into account, the agreement is much worse. The state 9¹, which is in weak Coriolis interaction with the states 6¹ and 7¹, allows us to see the effect of the interactions on the α -constants. They may be determined from the state 9¹ neglecting the interactions or taking them into

Table 8 Different ways to obtain the rotation–vibration interaction constants^a (in MHz) of the state $\nu_9 = 1$

	α_9^A	α_9^B	α_9^C
From the CCSD(T)_AE/TZ2Pf force field	13.292	3.681	−0.808
From 9 ¹ without interaction	1.997	8.649	−0.932
From 8 ¹ + 9 ¹ and 8 ¹	4.857	10.033	−0.314
From 9 ¹ with interactions ^b	29.885	10.446	−0.926
From 9 ¹ with interactions ^c	29.805	10.527	−0.924

^a The statistical uncertainty is only a few kHz. ^b Coriolis interactions with 6¹ and 7¹. ^c Coriolis interactions with 6¹, 7¹ and 8¹.

account. It is also possible to obtain them from the states 8¹ + 9¹ and 8¹. The results are given in Table 8 and confirm that the α -constants may vary considerably.

Another way to check the accuracy of the rovibrational corrections is to compare the experimental ground state rotational constants with those derived from the best *ab initio* structure, $r_e^{\text{BO}}(\text{I})$, and the *ab initio* rovibrational corrections. A still simpler and more powerful test is to look at the equilibrium inertial defects calculated from the semiexperimental equilibrium rotational constants. Ideally, they should be zero because the molecule is planar but, in most cases, they slightly differ from zero because of a systematic error in the rovibrational corrections. The results are shown in Table 9. It is obvious that there is a problem with the *A* and *B* rotational constants of the deuterated species because their residual, which is expected to be mainly systematic, is significantly different from that of the other isotopologues. Likewise, the semiexperimental inertial defect of the deuterated species has a sign opposite to that of the other species. Such a problem was expected and easy to explain.¹² The errors of the semiexperimental constants *A* and *B* of the deuterated species are of similar magnitude but of opposite sign, whereas their sum is almost the same for all species. It is due to a large rotation of the principal axis system (PAS) upon isotopic substitution that amplifies the errors of the rovibrational corrections, a typical difficulty of oblate tops. Fig. 3 clearly shows that there is an axis switching when going from BF₂OH to BF₂OD. It is also important

Table 7 Rotation–vibration interaction constants (MHz) for ¹¹BF₂OH

Mode	Interaction ^a	α_i^A		α_i^B		α_i^C	
		Exp. ^b	Cal. ^c	Exp. ^b	Cal. ^c	Exp. ^b	Cal. ^c
1	No	15.6	3.9	28.0	12.8	3.4	4.1
2	No	44.5	46.3	32.8	33.1	−15.5	−20.6
	ζ_{23}^c	44.2	46.3	33.8	33.1	41.9	23.0
3	No	—	36.1	9.8	44.2	62.3	67.3
	ζ_{23}^c	—	36.1	9.1	44.2	5.0	23.7
4	No	38.1	−8.6	−37.4	−8.3	3.8	3.7
	<i>d</i>	37.3	—	−38.4	—	4.9	—
5	No	19.7	19.4	19.1	19.3	10.2	10.0
6	No ^e	−10.0	−15.1	−9.2	−6.9	−49.7	−50.0
	ζ_{67}^c	−9.8	−15.1	−9.1	−6.9	22.7	3.9
7	No	6.2	4.8	−12.8	−18.8	56.1	55.8
	ζ_{67}^c	6.0	4.8	−12.9	−18.8	−16.3	1.9
8	No	1.0	−0.1	−3.2	−4.0	−7.3	−7.5
9	No	2.0	13.3	8.6	3.7	−0.9	−0.8
	<i>f</i>	29.8	—	10.5	—	−0.9	—

^a See text and Table 1. ^b This work and ref. 8 and 9. ^c CCSD(T)_AE/TZ2Pf value. ^d See text and Table 4. ^e Note that there is a good agreement for $\alpha_6^A + \alpha_6^B$. ^f See text and Tables 3 and 4.

Table 9 Semiexperimental rotational constants and their difference from the *ab initio* equilibrium ones (in MHz) and semiexperimental inertial defects (in uÅ²)

	¹¹ BF ₂ OH	¹⁰ BF ₂ OH	¹¹ BF ₂ OD	¹⁰ BF ₂ OD	¹¹ BF ₂ ¹⁸ OH	¹⁰ BF ₂ ¹⁸ OH
$A_e^{\text{SE } a}$	10 370.30	10 370.53	10 334.05	10 334.11	10 241.76	10 241.75
$B_e^{\text{SE } a}$	10 136.86	10 136.96	9446.32	9446.31	9543.99	9544.00
$C_e^{\text{SE } a}$	5126.15	5126.26	4935.06	4935.07	4940.37	4940.37
ΔA^b	4.04	4.05	2.03	1.99	3.23	3.21
ΔB^b	3.14	3.18	5.15	5.14	3.97	3.97
ΔC^b	1.82	1.85	1.80	1.79	1.90	1.90
$\Delta A + \Delta B$	7.18	7.23	7.18	7.13	7.19	7.19
Δ_e^c	−0.0006	−0.0009	0.0014	0.0014	−0.0017	−0.0018
δA^d	−0.003	−0.015	−1.762	−1.808	−0.010	−0.025
δB^d	−0.028	0.009	1.757	1.745	−0.026	−0.016
δC^d	0.022	0.048	0.010	−0.005	0.072	0.078

^a Semiexperimental equilibrium rotational constants. ^b Difference between the semiexperimental value and the value calculated from the $r_e^{\text{BO}}(\text{I})$ structure from Table 6. ^c Semiexperimental equilibrium inertial defect. ^d Residuals of the fit, last column of Table 6.



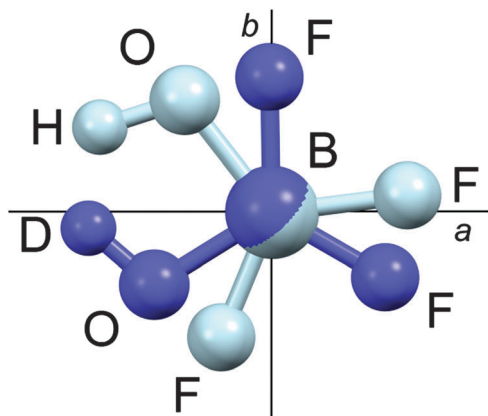


Fig. 3 $^{11}\text{BF}_2\text{OH}$ and $^{11}\text{BF}_2\text{OD}$ in their superposed principal axis systems.

to notice that the equilibrium inertial defect is much worse when any computed α -constants are replaced by their experimental values.

6.3. Determination of the structure

There is no isotopic substitution available for fluorine. The boron atom is close to the center of mass, $a(^{11}\text{B}) = 0.019 \text{ \AA}$ and $b(^{11}\text{B}) = -0.034 \text{ \AA}$; thus, the substitution $^{11}\text{B} \rightarrow ^{10}\text{B}$ does not bring any new information. Furthermore, we have seen in the previous section that the A and B rotational constants of the deuterated species are affected by a rather large systematic error. Therefore, the available rotational constants do not allow us to determine a complete structure. To overcome this difficulty, the method of mixed regression may be used.^{42–44} This method, also called the predicate method, uses simultaneously equilibrium moments of inertia and bond lengths and bond angles from high-level quantum chemical calculations in the structure fitting. However, it is useful for large molecules only if reliable predicates may be estimated without using the expensive CCSD(T) method. Actually, it is known that the OH bond length can be estimated at the MP2 level using either the cc-pVTZ or the cc-pVQZ basis sets with an uncertainty less than 0.002 \AA .⁴⁵ On the other hand, the prediction of an accurate CF bond length is difficult. Nevertheless, it is easy to obtain an accurate value of the difference $r(\text{CF}_{\text{syn}}) - r(\text{CF}_{\text{anti}})$ at the MP2/cc-pVQZ level; see Table S1 of the ESI.† Finally, the bond angles may be estimated at the MP2/6-311+G(3df,2pd) level of theory with an uncertainty of about 0.2° .⁴⁶ Different combinations of predicates were tried. A fit with three predicate values, [$r(\text{OH})$, $r(\text{BF}_{\text{syn}}) - r(\text{BF}_{\text{anti}})$ and $\angle(\text{BOH})$], gives extremely good results; see Table 8. However, it is also possible to obtain a very satisfactory fit with only two predicate values as shown in Table 6. Yet, it has to be noted that, when $r(\text{BF}_{\text{syn}}) - r(\text{BF}_{\text{anti}})$ is not used as a predicate, the fit is ill-conditioned with a large condition number, high correlation between the parameters and larger standard errors for the parameters. This result is simply due to the fact that there is not enough information to accurately determine the position of the fluorine atoms. On the other hand, the information given by the two predicates $r(\text{OH})$ and $\angle(\text{BOH})$ is somewhat redundant.

Obviously, the predicates play a leading role in increasing the accuracy of the parameters, but it is possible to check their influence by reducing their weight. In the particular case of BF_2OH , it does not significantly modify the parameters, but it increases their standard deviation as well as the condition number. Actually, the best guaranty of the compatibility of the predicates with the semiexperimental moments of inertia is an analysis of the residuals. The best semiexperimental structure is given in the last column of Table 6.

7. Conclusions

The *ab initio* calculation of the anharmonic force field and the analysis of the high-resolution infrared spectrum shows that almost all fundamental states are perturbed, even the lowest one. The only exception is the 5^1 state which does not appear to be perturbed although it is in Fermi resonance with the extremely close 7^2 state. This lack of mixing is due to the fact that the cubic force constant φ_{577} is vanishingly small. When the perturbation is small and can thus be neglected, there is a satisfactory agreement between the experimental rotation–vibration interaction constants and the values calculated from the force field. On the other hand, when the perturbations are taken into account in the analysis of the experimental spectra, the agreement becomes disappointing. This difficulty is rather frequent, HCOOH being another well studied example.²⁰ In particular, for planar molecules, the equilibrium inertial defect, Δ_e , is closer to zero when calculated from the semiexperimental constants. For instance, in the case of HNO_3 ,²² $\Delta_e = 0.0002 \text{ u\AA}^2$ with the semiexperimental rotational constants and $\Delta_e = 0.0069 \text{ u\AA}^2$ when the available experimental α 's replace the *ab initio* ones. It might be tempting to think that, in the presence of interactions, the system of normal equations becomes ill-conditioned and, therefore, the derived parameters are not accurate. However, fixing the non-diagonal interaction parameters to the *ab initio* values does not significantly improve the situation. Another possible explanation is that the levels may be affected by anharmonic resonances, even if they are far away as was shown by Saito in the particular case of SO_2 .⁴⁷ However, the provisional conclusion is that there is no obvious explanation.

Another interesting result of this study is that the large amplitude motion of the OH group does not hinder an accurate determination of the semiexperimental structure. In the particular case of BF_2OH , there are two problems: there is not enough experimental data because there is no isotopic substitution available for the fluorine atoms and the boron atom is extremely close to the center of mass; therefore, its substitution does not bring any useful information. Furthermore, BF_2OH is an oblate top with the moment of inertia I_c much larger than the other two moments of inertia, I_a and I_b . Molecules of this shape experience a large rotation of the principal axis system upon certain isotopic substitutions. For such isotopologues it is difficult to obtain a good structural fit to the semiexperimental moments of inertia, I_a and I_b . To achieve an accurate structure, the mixed estimation method is used. In this method, internal coordinates of good



quality quantum chemical calculations (with appropriate uncertainties) are fitted simultaneously with the semiexperimental moments of inertia of all isotopologues.

A very accurate *ab initio* structure can be obtained either by direct optimization at the convergence limit, CCSD(T)_AE/cc-pwCVQZ, or by the less expensive additive method based on the CCSD(T)_AE/cc-pwCVTZ structure improved by small corrections to the convergence limit calculated at the MP2 level. In any case, the core–core and core–valence correlation effects have to be taken into account in the accurate structure calculations because they are very large (≈ 0.003 Å for BF and BO bond lengths).

Appendix: Hamiltonian

The ν -diagonal block is a standard Watson Hamiltonian in A-reduction and representation I^r . However, for BF₂OH, the ν_4 mode (OH in plane bending) and the ν_9 mode (OH-torsion relative to the BF₂ moiety) are large amplitude motions.⁹ As a consequence, for each of the $\{4^1, 7^1, 9^1, 6^1, 7^1, 9^2, 6^1, 9^1\}$ interacting states the ν -diagonal blocks also include an \mathbf{XZ}_ν , non-orthorhombic operator

$$\mathbf{XZ}_\nu = h_{xz}^\nu \{\hat{J}_x \hat{J}_z\} + \dots \quad (\text{A1})$$

with

$$\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A} \quad (\text{A2})$$

These \mathbf{XZ}_ν , non-orthorhombic operators account for the rather strong Coriolis interactions linking the two 4^1 bending or (9^2 torsional) sub-states. In addition the tunnelling splittings due to the large amplitude OH bending (for the ν_4 band) or OH torsion (for the $2\nu_9$ band) had to be accounted for by specific bending or torsional operators in the 4^1 and 9^2 vibrational blocks. As in ref. 9 and 48, these operators written in the internal axis method (IAM)-like approach involve matrix elements of the $D(\chi, \theta, \varphi)$ Wigner operators, where χ , θ and φ are the Euler angles, with $\chi = \varphi + \pi$ for symmetry considerations

$$\begin{aligned} \langle JK'\gamma' | \hat{H} | JK''\gamma'' \rangle = \varepsilon(-1)^{K'} & \left(\cos((K' + K'')\varphi) d_{K', K''}^{(J)}(\theta) \right. \\ & \left. + \gamma'' \cos((K' - K'')\varphi) d_{K', -K''}^{(J)}(\theta) \right) \end{aligned} \quad (\text{A3})$$

The elements off-diagonal in ν include Coriolis operators

A-type Coriolis:

$${}^{\nu, \nu} \hat{A} = {}^{\nu, \nu} A_z \hat{J}_z + {}^{\nu, \nu} A_{xy} \{i\hat{J}_x, i\hat{J}_y\} + \dots \quad (\text{A4})$$

B-type Coriolis:

$$\begin{aligned} {}^{\nu, \nu} \hat{B} = {}^{\nu, \nu} B_x \hat{J}_x + {}^{\nu, \nu} B_{yz} \{i\hat{J}_y, \hat{J}_z\} + {}^{\nu, \nu} B_{xj} \hat{J}_x \hat{J}_z^2 \\ + {}^{\nu, \nu} B_{xzz} \{\hat{J}_z^2, \hat{J}_x\} + {}^{\nu, \nu} B_{x3} (\hat{J}_+^3 + \hat{J}_-^3) \end{aligned} \quad (\text{A5})$$

with

$$\hat{J}_\pm = \hat{J}_x \mp i\hat{J}_y \quad (\text{A6})$$

C-type Coriolis:

$${}^{\nu, \nu} \hat{C} = {}^{\nu, \nu} C_y i\hat{J}_y + {}^{\nu, \nu} C_{xz} \{\hat{J}_x, \hat{J}_z\} \quad (\text{A7})$$

as well as Fermi and anharmonic terms

$${}^{\nu, \nu} \hat{A}nh = {}^{\nu, \nu} Anh_0 + {}^{\nu, \nu} Anh_{xy} \hat{J}_{xy}^2 + {}^{\nu, \nu} Anh_{xyz} \{\hat{J}_z^2, \hat{J}_{xy}^2\} \quad (\text{A8})$$

with

$$\hat{J}_{xy}^2 = \hat{J}_x^2 - \hat{J}_y^2 \quad (\text{A9})$$

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