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RbBrF₄ revisited

Sergei Ivlev,^[a,b] Antti Karttunen,^[c] Roman Ostvald,^{*[b]} and Florian Kraus^{*[a]}**Keywords:** Tetrafluoridobromate; Rubidium; Powder X-ray diffraction; Crystal Structure; DFT

Rubidium tetrafluoridobromate(III) was synthesized and structurally characterized. The compound is isotopic to sodium and potassium tetrafluoridobromate(III), and crystallizes in the tetragonal space group *I4/mcm* (*tI24*, KBrF₄ structure type) with $a = 6.3718(2)$, $c = 11.4934(3)$ Å, $V = 466.63(2)$ Å³, $Z = 4$, at $T = 293$ K.

Additionally we investigated the compound by means of IR- and Raman spectroscopy as well as theoretical investigations. The data obtained by quantum chemical calculations confirm the crystal structure, and also the atomic distances and angles with an average deviation of 2.2 to 2.7%.

* Prof. Dr. Florian Kraus

Fax: +49 6421 28 - 26 66 8

E-Mail: florian.kraus@chemie.uni-marburg.de

* Prof. Dr. Roman Ostvald

Fax: +7-3822-419-801

E-Mail: ostvald@tpu.ru

[a] Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany

[b] Tomsk Polytechnic University, Institute of Physics and Technology, Rare, Scattered and Radioactive Element Technology Department, 30 Lenina avenue, Tomsk, 634050, Russia

[c] Department of Chemistry, Aalto University, 00076 Aalto, Finland

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Introduction

Alkali and alkaline earth metal tetrafluoridobromates(III), Mⁿ⁺(BrF₄)_n, may be perspective fluorinating agents in various fields of chemistry and chemical technology. Recent studies^[1-7] showed for example their potential use for the recycling of noble metals, the so called “urban mining”. The exceptional oxidative and fluorinating ability of the tetrafluoridobromates(III) allows even the conversion of the most inert noble as well as refractory metals into compounds for further “classical” extraction and separation procedures.

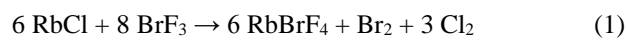
It is interesting to note that the physical and chemical properties of some tetrafluoridobromates(III) are still not fully established, whereas some others, mainly KBrF₄ and Ba(BrF₄)₂ are well documented.^[8-14] The single crystal structures of KBrF₄^[15-17], RbBrF₄^[8], and CsBrF₄^[12] have been determined. Single crystal structures are not only of purely theoretical interest but are a precondition to obtain technologically important parameters by computer simulations, such as the values of thermodynamic functions (enthalpy of formation, entropy, heat capacity, etc.) at given temperatures, or to assess the stability, solubility and reactivity of the compounds. It was reported for RbBrF₄ that the rubidium atoms occupy the special position 4c (0; 0; 0) of the space group *I4/mcm*.^[8,9] This leads to a square prismatic coordination of the Rb atoms, which is in contrast to the K⁺ coordination of KBrF₄. There, the cations reside on the special position 4a (0; 0; ¼), thus a square antiprismatic

coordination is obtained.^[15-19] As rubidium salts are often isotopic to the respective potassium salts, we reinvestigated the crystal structure of RbBrF₄.

Results and Discussion

Synthesis of RbBrF₄

Rubidium tetrafluoridobromate(III) is obtained by the following, idealized but plausible, reaction equation 1:



The reaction is carried out in a PTFE test tube with the addition of a protective layer of Freon-113, which is inert to the reactants as well as the products. Moreover, it acts as a heat absorber and thus prevents the evaporation of BrF₃. The details of this technique were reported in our previous works^[7,12,13] and elsewhere^[2,10].

In order to prevent the formation of rubidium heptafluoridobromate(III), RbBr₂F₇ (which is possible due to the formation of regions with a local excess of liquid BrF₃, similarly to the case of CsBr₂F₇^[12]), a small excess of RbCl (3% by mass of RbCl) is used. The synthesized solid product appears as a white crystalline powder, which slowly hydrolyzes on moist air releasing bromine vapors, HF and presumably O₂.

According to quantitative X-ray fluorescence analysis using rubidium bromide as a standard, the mass ratio of Rb:Br in the product was equal to 1:1.22 due to the slight excess of Rb in the synthesis. This is equivalent to ~2.9% (by mass of RbCl), and is in good agreement with the 3% used in excess.

Powder X-Ray Diffraction Study on RbBrF₄

The powder X-ray diffraction pattern of the sample measured at 293 K is shown in Figure 1.

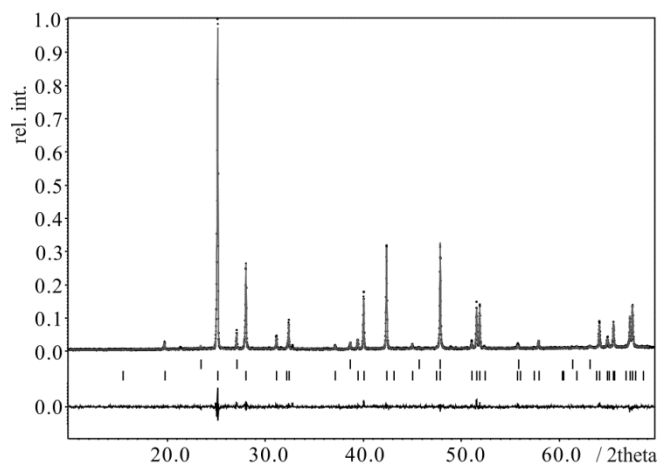


Figure 1. Powder X-ray diffraction pattern of RbBrF₄ at 293 K: the experimental data (black crosses), the Rietveld profile (grey), and the differential profile (bottom, black). The calculated reflection positions are shown as black ticks (the first row for RbCl, the second row for RbBrF₄).

Despite the presence of some unreacted RbCl, as indicated by the reflections of small intensities, there are no significant reflection overlaps, which make the powder pattern easily suitable for Rietveld refinement.

The obtained diffraction pattern can be indexed in the tetragonal crystal family with the lattice parameters $a = 6.3718(2)$, $c = 11.4934(3)$ Å, $V = 466.63(2)$ Å³. The observed reflection extinction conditions pointed to a body-centered lattice and the manual analysis of the extinction conditions narrowed the possible choice of space groups down to $I4cm$ (No. 108), $I4^-c2$ (No. 120) and $I4/mcm$ (No. 140). Since the RbBrF₄ crystal structure is not expected to be non-centrosymmetric and also taking the structures of NaBrF₄ and KBrF₄ into account, the Rietveld refinement of rubidium tetrafluoridobromate(III) was performed in the space group $I4/mcm$ (No. 140). Additionally, structure solutions using the SUPERFLIP algorithm^[20] yielded the same space group. It should be noted that the obtained cell parameters are in good agreement with the ones published in^[8]. Further details of the attempted refinement in the other two space groups are given in the Supporting Information.

The measured pycnometric density of RbBrF₄ is 3.33 ± 0.01 g/cm³, and thus Z is equal to 4.

The value of the crystallographic density is 3.43 g/cm³, which fits nicely to the experimentally determined value. Moreover, if the mass ratio of RbBrF₄:RbCl is calculated using the Rietveld method (96.5% : 3.5%), the theoretical density for the mixture would be 3.40 g/cm³, which is even closer to the experimentally observed value.

The crystallographic details for RbBrF₄ are shown in Table 1.

Table 1. Crystallographic details for RbBrF₄ at 293 K.

Property	Value
Empiric formula	RbBrF ₄
Color and habitus	white powder
Molar mass, g/mol	241.4
Crystal system	tetragonal
Space group	$I4/mcm$
a , Å	6.3718(2)
c , Å	11.4934(3)
V , Å ³	466.63(2)
Z	4
ρ_{exp} , g/cm ³	3.33 ± 0.01
$\rho_{Rietveld}$, g/cm ³	3.40
$\rho_{calc.}$, g/cm ³	3.43
λ , Å	1.540598 (Cu-K α_1)
T , K	293
R_p , wR_p	0.0900, 0.1188
$R(F^2)$ (all data), $wR(F^2)$ (all data)	0.0332, 0.0312
No. of data points, parameters, constraints, restraints	3975, 28, 0, 0
2θ range measured (min; max; increment)	10.000; 69.610; 0.015
2θ range refined (min; max; increment)	10.000; 69.610; 0.015

Crystal Structure of RbBrF₄

The structure solution was carried out manually and also using the SUPERFLIP algorithm implemented in Jana2006^[20], the structure refinement was carried out with the Jana2006 software^[21]. A section of the structure is shown in Figure 2, and the crystal structure in Figure 3.

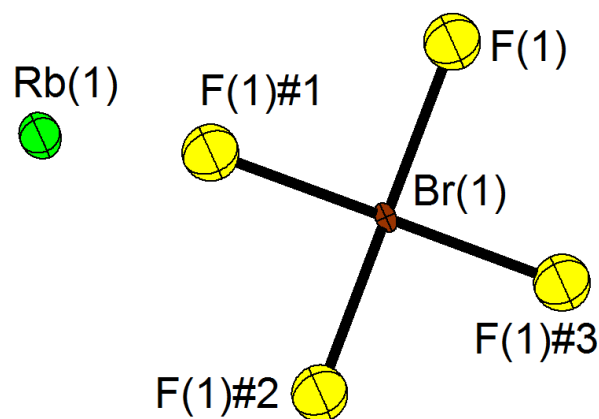


Figure 2. Cation and anion of RbBrF₄. Thermal ellipsoids are shown at 70% probability at 293 K, fluorine atoms are shown isotropic. Symmetry transformations for the generation of equivalent atoms: #1 $-1/2+y, 1/2+x, -z$; #2 $1/2-y, 1/2-x, -z$; #3 $-x, 1-y, z$.

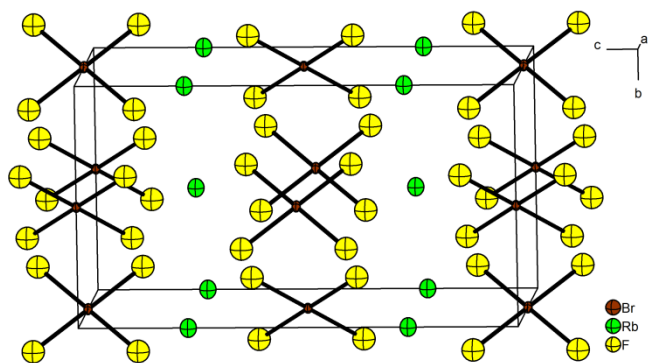


Figure 3. The crystal structure of RbBrF₄. Thermal ellipsoids are shown at 70% probability level at 293 K. Fluorine atoms are shown isotropic.

The rubidium atoms occupy the *Wyckoff* position 4*a*, and the square planar BrF₄⁻ anions with their bromine atoms the *Wyckoff* position 4*d*. This arrangement makes the structure chemically more plausible and isotopic to KBrF₄ of which the structure was previously well-characterized using also neutron diffraction^[15].

The location of the Rb atoms on the special position 4*a* leads to a square-antiprismatic coordination by F-atoms, with Rb–F distances of 2.851(7) Å. This value nicely agrees to the Rb–F distance observed in the isotopic compound RbAuF₄ with 2.85(2) Å. Square (sometimes distorted) prismatic coordination spheres of Rb atoms are frequent, e.g. as observed in the compounds RbBiF₄, RbAlF₄, RbFeF₄, with mean Rb–F distances of 2.3846, 2.918(1), and 2.98(1) Å, respectively. The experimentally determined Br–F distance in the title compound is 1.932(8) Å, which is very close to the values observed for KBrF₄ with 1.89(1) Å^[15], for CsBrF₄ with 1.94(4) to 1.97(4) Å^[12], for CsBr₂F₇ with 1.7686(11) to 2.1431(12) Å^[12], for Ba(BrF₄)₂ with 1.801(4) to 1.935(2) Å^[13], and also to the bond lengths observed for BrF₃ molecules in the gas phase with 1.721 to 1.810 Å (no s.u. given)^[22,23] and the BrF₃ molecules in their crystal structure with 1.71(1) to 1.888(9) Å^[24], as well as to the theoretically predicted Br–F distance in the isolated BrF₄⁻ anion (1.8994 Å)^[25].

If we carry out the refinement using the "old" model of the crystal structure on our powder pattern (with the Rb atom on the 4*c* position) the Rietveld refinement produces very bad agreement factors: $R_p = 0.4527$, $wR_p = 0.5848$, $R(\text{obs}) = 0.6004$, $wR^2(\text{obs}) = 0.5580$, $R(\text{all}) = 0.6522$, $wR^2(\text{all}) = 0.5669$. Additionally, the accuracy of the lattice parameters is one order of magnitude less with $a = 6.372(2)$, $c = 11.497(7)$ Å, $V = 466.8(4)$ Å³, and for example in the BrF₄⁻ anion the atomic distances are too long with 2.1031(8) Å and its angles are 100.727(12) and 79.273(7)°. Furthermore, the isotropic displacement parameters of the Rb and Br atoms refined to negative values. Therefore the structure model with the Rb atom on the 4*a* position is clearly preferred over the "old" model.

Computational Study

In order to have a deeper insight into the structure of RbBrF₄, we carried out a full structural optimization of the

cell parameters and atomic positions of the previously reported and the crystal structure described here. The optimization was done within space group *I4/mcm* and the DFT-PBE0/SVP level of theory (see Experimental Section for Computational Details). The cell parameters as well as the selected bond distances and angles for both structures are shown in Table 2. Optimized and experimentally observed atom positions for both structures are given in Table S1 and Table S2 (Supporting Information).

Table 2. Experimental and calculated cell parameters and selected atomic distances / angles for RbBrF₄. The symmetry operations used for the generation of the equivalent atoms are not shown because the original structures were slightly modified for comparative reasons.

Parameter	RbBrF ₄ (from lit. [8])		RbBrF ₄ (this study)	
	exp.	calc.	exp.	calc.
a , Å	6.351(6)	6.94	6.3718(2)	6.20
c , Å	11.489(10)	8.93	11.4934(3)	11.74
V , Å ³	463.41(96)	430.8	466.63(3)	451.5
Br–F, Å	1.8903(32)	1.91	1.932(8)	1.91
Rb–F, Å ^{<i>a</i>}	2.7653(33)	2.94	2.851(7)	2.84
F–Br–F ^{*, ° <i>b</i>}	89.861(128)	82.7	90.4(3)	89.7
F–Br–F ^{**, ° <i>c</i>}	90.1(1)	97.3	89.6(3)	90.3

^{*a*} – the shortest distance; ^{*b*} – two F-atoms along the *c*-axis; ^{*c*} – two F-atoms along the diagonal between the *a*- and *b*-axes.

According to the obtained results the interatomic distances of both structures are comparable with those observed in other tetrafluoridobromates(III)^[10,12,13,15]. However, the bond angles of the BrF₄⁻ anion of the previously reported structure show a strong distortion from the expected square-planar arrangement. Moreover, the calculated cell parameters deviate by 9.3% (for *a*) and 22.3% (for *c*) from the experimentally determined values, whereas the structure described here shows a nice correlation between theory and experiment with an average difference of ~2.5%. These facts additionally indicate that the rubidium atoms occupy the special position 4*a* inside the lattice of RbBrF₄.

Vibrational spectroscopy

After conducting a full geometry optimization the IR- and Raman spectra for both optimized structures were calculated and are shown in Figure 4.

The calculated spectra for the structures determined here and in^[8] appeared to be very similar to each other, which may be expected since the spectra are mostly determined by the chemical bonding inside the BrF₄⁻ anions. But in spite of that there are clearer differences in the lower wavenumbers due to the differences in the overall structures. Therefore, we carried out the experimental measurements of the IR- and Raman spectra of RbBrF₄ (Figure 5).

The Raman spectrum shows a good correlation of the wavenumbers and the relative intensities with the calculated one, although, the band positions are slightly shifted (see the Supporting information for detailed analysis of the Raman spectrum). The theoretically calculated Raman spectrum for the RbBrF₄ structure with the Rb atom on the 4*c* Wyckoff position^[8] shows clear differences with respect to the experimentally observed spectrum: an additional band at 282 cm⁻¹, no band corresponding to the experimentally observed band at 241 cm⁻¹, and poor agreement with the

experimentally observed band features at around 100 cm^{-1} . In summary, the predicted Raman spectrum supports the revised structure with the Rb atom on the $4a$ Wyckoff position.

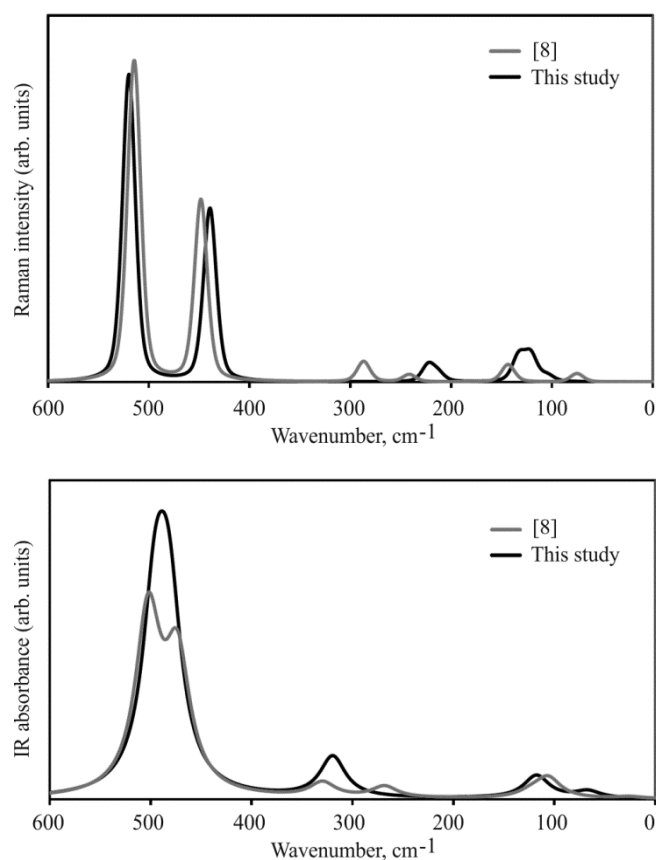


Figure 4. The theoretically predicted vibrational spectra of RbBrF₄.

The features of the IR spectrum are also in sufficient correspondence with the results of the *ab initio* calculations, although the sample-dependent shapes of the bands could not be predicted (see Supporting information for detailed analysis of the IR spectrum). The sharp extra band at 177 cm^{-1} can be attributed to RbCl which is intentionally present (see Supporting information). Since the theoretical IR peak positions are rather similar for both crystal structures and the predicted intensities are in both cases so different from the experiment, the theoretical IR spectra are not as useful for differentiating the two crystal structures as the Raman spectra.

All Raman and IR bands can be readily assigned to the definite vibrational modes according to the information available in the literature (see Supporting information)^[10]. In order to check if there are also mode combinations mentioned in the literature^[10], we recorded the full IR spectrum shown in Figure S1 (Supporting Information).

In general, it can be noted that the predicted Raman spectra are more favourable towards the structure presented here rather than to the previously reported one.

Conclusions

Polycrystalline samples of rubidium tetrafluorobromate(III) RbBrF₄ were directly synthesized from RbCl and BrF₃. The compound crystallizes in the tetragonal space group *I4/mcm* with $a = 6.3718(2)$, $c = 11.4934(3)\text{ Å}$, $V = 466.63(2)\text{ Å}^3$, and $Z = 4$ at 293 K. The cell parameters are in a good correspondence with the ones published previously^[8]. However, the elucidated crystal structure is different in terms of the Rb atom position. We observe the occupation of the $4a$ Wyckoff position in contrast to the previously reported occupation of the $4c$ position. This finding is supported by the additional theoretical and IR/Raman spectroscopic investigations. Also, the crystal structure of RbBrF₄ reported here is isotopic to the well-characterized potassium tetrafluorobromate(III) KBrF₄.

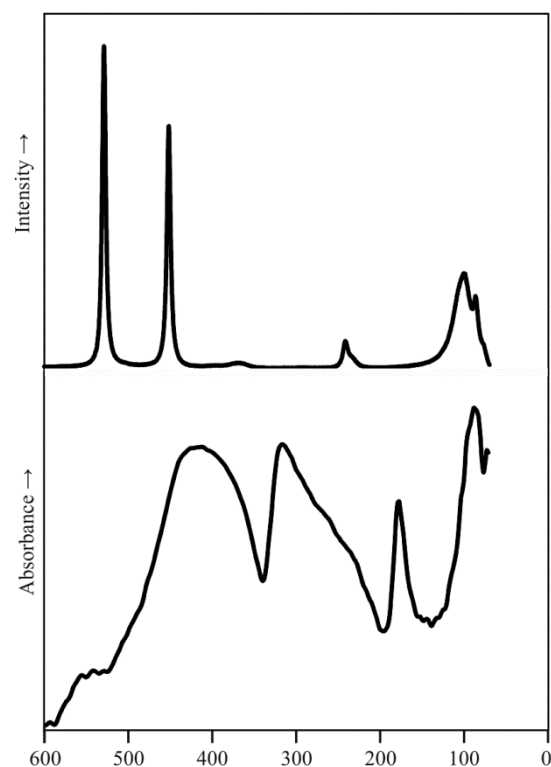


Figure 5. Measured Raman (top) and IR (bottom) spectra of RbBrF₄.

Experimental Section

General: All operations with RbBrF₄ were carried out in an atmosphere of dry and purified argon (Westfalen AG, Germany), so that a possible contact of the substances with moisture or air was minimized ($\text{O}_2 < 1\text{ ppm}$, $\text{H}_2\text{O} < 1\text{ ppm}$). RbCl (“chemically pure” grade, JSC Vekton, Russia) was used without further purification. BrF₃ was synthesized by slowly passing gaseous fluorine through liquid bromine in a nickel reactor with continuous cooling^[26,27]. After completion of the reaction, BrF₃ was distilled, and only the fraction with b.p. = 125 °C was used for the experiments. Then, RbCl and BrF₃ were used for the preparation of RbBrF₄.

Preparation of RbBrF₄: RbCl (2.71 g, 22.5 mmol, 1.03 equiv.) with an excess of 0.7 mmol (3% by mass) was placed in a PTFE

tube and layered with Freon-113 (15 mL). Liquid BrF₃ (3.99 g, 29.1 mmol, 1.00 equiv.) was added dropwise under vigorous stirring. More portions of Freon-113 were added as needed. The total yield of dry product was 5.26 g (consisting of 0.18 g RbCl (1.5 mmol) and 5.08 g RbBrF₄ (21.1 mmol, 96.5% of theory) – an estimation calculated using the Rietveld method. More details of the quantitative analysis of the product are given in the *Results and Discussion* section.

X-ray Fluorescence Analysis: The energy dispersive X-ray fluorescence analysis (EDXRF) was carried out with an ARL QUANT'X spectrometer (Thermo Scientific, USA) equipped with a Peltier-cooled Si(Li) detector. The measurements were done under the most suitable experimental conditions in order to obtain the primary lines for both rubidium and bromine: a thick Pd filter with a voltage of 28 kV on the X-ray tube. The duration of one measurement was equal to 120 s of lifetime. All measurements were done in air with the samples introduced in the form of aqueous solutions after the hydrolysis of RbBrF₄ with distilled water in a sealed PTFE container. The sample holders were covered with thin layers of Prolene® Film (Chemplex Industries, USA).

Density Measurement Details: The density of RbBrF₄ was measured using the automated gas displacement pycnometry system AccuPyc II 1340 (Micromeritics, Germany) using a calibrated 0.1 cm³ sample holder and helium as the gas being displaced. The number of preliminary purges was set to 30, while the subsequent density measurements were done 100 times with further averaging.

Powder X-ray Diffractometry: Powder X-ray diffraction patterns were obtained with a Stadi-P-Diffractometer (Stoe, Germany) by using Cu-K_{α1} radiation, a germanium monochromator, and a Mythen1K detector. The compound was filled into a dry 0.3 mm Lindemann capillary and flame-sealed. The data were handled and indexed using WINXPOW software [28].

Structure Solution and Refinement Details: The profile fitting, structure solution and Rietveld refinement on *F*² using the Berar correction were done with the Jana2006 software [21]. The peak profile shape was described by the pseudo-Voigt function. The background was approximated with the Chebyshev polynomial with nine terms. The scale factor, zero shift, profile shape parameters, lattice parameters, and atom coordinates together with their displacement parameters (Rb and Br anisotropically, F isotropically) were refined. No absorption correction was applied.

Further details of the crystal structure investigations are available from the Fachinformationzentrum Karlsruhe, Germany, 76344 Eggenstein-Leopoldshafen (Germany), <http://www.fiz-karlsruhe.de/icsd.html>, on quoting the depository number CSD-430102.

IR and Raman Spectroscopy: The IR spectra of RbBrF₄ were recorded using a Bruker Tensor 37 FTIR spectrometer with a far-infrared ATR-module, and the OPUS software package [29]. Due to sample manipulations on air, some hydrolysis of RbBrF₄ might have taken place, although the authors tried to find a compromise between the measurement time and the spectrum quality. The full range of 4000-360 cm⁻¹ IR spectrum was measured on a Bruker Alpha FTIR spectrometer under an Ar atmosphere. The Raman spectra were collected using a Labram HR 800 (JobinYvon)

instrument equipped with a He/Ne laser tube ($\lambda = 632.817$ nm). The samples of RbBrF₄ were prepared in flame-sealed glass capillaries under Ar, and the collected data were handled by the LabSpec software.

Computational Details: The structural and spectroscopic properties of RbBrF₄ were investigated using the CRYSTAL14 program package [30,31]. Both the atomic positions and lattice parameters were fully optimized using the PBE0 hybrid density functional method [32,33]. Split-valence + polarization (SVP) level basis sets were applied for all atoms (see Supporting information for additional basis set details).^[Basis] The reciprocal space was sampled using a 6x6x6 Monkhorst-Pack-type *k*-point grid [34]. For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used. Default optimization convergence thresholds and DFT integration grids applied in all calculations. The harmonic vibrational frequencies [35,36], IR intensities [37], and Raman intensities [38,39] were obtained by using the computational schemes implemented in CRYSTAL.

Supporting Information (see footnote on the first page of this article): The optimized and experimentally determined atom positions for RbBrF₄, the full-range IR spectrum and additional computational details.

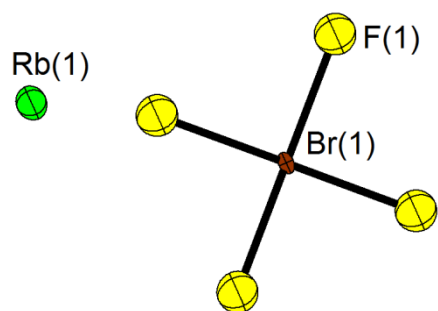
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