# Hydrogen Bonding in Potassium Fluoride Dihydrate: A Crystallographic, Spectroscopic, and Theoretical Study

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Crystal structure data of orthorhombic $KF{\cdot}2H_2O$ are reported that were obtained from neutron diffraction refinements at 295 K ($Pmc2_1$; $Z = 2$; $a = 4.082(2)$ Å, $b = 5.182(2)$ Å, $c = 8.825(5)$ Å; $R = 0.020$) and from X-ray diffraction refinements at 298 and 120 K ($R = 0.018$ and 0.009, respectively). Each of the two independent water molecules is coordinated by two potassium ions and forms two O−H···F hydrogen bonds (neutron values: O−H = 0.966–0.971 Å, H···F = 1.752–1.796 Å, and O···F = 2.719–2.753 Å). Vibrational spectra of partially deuterated samples yielded three rather similar uncoupled $\bar{\nu}$(OD) frequencies (2462, 2478, and 2491 $cm^{-1}$ at 75 K) in agreement with the three crystallographically different, but geometrically similar O−H···F hydrogen bonds. Energy band calculations have been performed using the LAPW method. Total and partial densities of states show that the water−potassium interactions are almost exclusively electrostatic, while the hydrogen bond interactions with the fluorine anions have additional covalent contributions or at least polarization effects of about 20%.

## Introduction

Some years ago the structural and spectroscopic data on hydrates in the literature were surveyed and frequency−distance correlations established for O-H···Y (Y = N, O, S, Se, Cl, Br, I) hydrogen bonds[1] of more than 50 compounds. However, no frequency distance correlation for O−H···F hydrogen bonds could be established, mainly because almost no suitable spectroscopic data were available. Meanwhile this situation has been slightly improved because for $ZnF_2{\cdot}4H_2O$, beside the necessary structural data,[2,3] suitable spectroscopic data[4] became available in the literature.

In this paper we describe combined structural, vibrational spectroscopic, and theoretical investigations of $KF{\cdot}2H_2O$, a representative member of the class of salt hydrates containing O−H···F hydrogen bonds. The basic features of its crystal structure were known from an early X-ray study:[5] space group $Pmc2_1$, $a = 4.06$ Å, $b = 5.15$ Å, $c = 8.87$ Å, and $Z = 2$; the unit cell contains two independent water molecules, which are tetrahedrally coordinated by two potassium cations and two fluorine anions. Since this early work yielded only approximate lattice constants and coordinates of the heavier atoms, an up-to-date determination of the structure was highly desirable to provide accurate geometric data for the two water molecules and their environments. Results of such structure refinements are reported. IR and Raman spectroscopic data in particular the $\bar{\nu}$(OD) stretching frequencies of isotopically dilute HOD molecules provide vibrational spectroscopic information about hydrogen bonded water molecules.[1,6,7] A frequency−distance correlation of O−H(D)···F hydrogen bonds is given, including data of $ZnF_2{\cdot}4H_2O$. While most salt hydrates are too complicated to perform quantum mechanical calculations the present system is sufficiently simple to study its band structure using the linear augmented plane wave (LAPW) method.[8] This is a novel approach for a better understanding of the bonding of water molecules in crystalline solids and extends previous work on simple ionic crystals, such as oxides and fluorides.[9] The character of the hydrogen bond and total energy results are related to vibrational spectroscopic data.

## Experimental and Computational Aspects

**Crystal Growth.** According to the phase diagram of $KF-H_2O$,[10] the hydrate $KF{\cdot}2H_2O$ forms on crystallization from aqueous solutions with about 44–62 wt % KF in the temperature range 19–41 °C. At lower temperatures the tetrahydrate, $KF{\cdot}4H_2O$, is formed, while at temperatures above 41.4 °C anhydrous KF is obtained. In our work,

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(1) Mikenda, W. *J. Mol. Struct.* **1986**, *147*, 1.

(2) Butvetskii, B. V.; Nozik, Yu. Z.; Fykin, L. E.; Polishchuk, S. A.; Laptash, N. M. *Koord. Khim.* **1977**, *3*, 1594.

(3) Zottl, M.; Mereiter, K.; Preisinger, A. *Z. Kristallogr.* **1992**, *Suppl. 6*, 493.

(4) Swanepoel, J.; Heyns, A. M. *Spectrochim. Acta* **1991**, *47A*, 1595.

(5) Anderson, T. H.; Lingafelter, E. C. *Acta Crystallogr.* **1951**, *4*, 181.

(6) Falk, M.; Knop, O. In *Water—A Comprehensive Treatise*; Franks, F. (Ed.) Plenum Press: New York, 1973; Vol. 2, Chapter 2. Lutz, H. D. *Struct. Bonding (Berlin)* **1988**, *69*, 97.

(7) Berglund, B.; Lindgren, J.; Tegenfeldt, J. *J. Mol. Struct* **1978**, *43*, 179.

(8) Blaha, P.; Schwarz, K.; Augustyn, R. WIEN93, Technical University of Vienna, 1993. (An improved and updated Unix version of the original copyrighted WIEN code, which was published by: Blaha, P.; Schwarz, K.; Sorantin, P. I.; Trickey, S. B. *Comput. Phys. Commun.* **1990**, *59*, 399).

(9) Sorantin, P.; Schwarz, K. *Inorg. Chem.* **1992**, *31*, 567.

(10) Magin, R. L.; Mangum, B. W.; Statler, J. A.; Thornton, D. D. *J. Res. Natl. Bur. Stand. (U.S.)* **1980**, *86(2)*, 181–192.

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**Table 1.** Crystallographic Data for KF·$2H_2O$

| | neutron diffr | X-ray diffr | |
|---|---|---|---|
| cryst sample | 2 rounded blocks | sphere, 0.45 mm diam. | |
| cryst data | | | |
| formula | KF·$2H_2O$ | | |
| fw | 94.127 | | |
| cryst syst | orthorhombic | | |
| space group | $Pmc2_1$ (No. 26) | | |
| $T$, °C | 22 | 25 | −153 |
| $a$, Å | 4.082 (2) | 4.083 (1) | 4.062 (1) |
| $b$, Å | 5.182(2) | 5.184(1) | 5.157(1) |
| $c$, Å | 8.825(5) | 8.831(1) | 8.778(2) |
| $V$, Å$^3$ | 186.7(5) | 186.92(6) | 183.88(7) |
| Z | 2 | 2 | 2 |
| $\varrho_{calcd}$, g cm$^{-3}$ | 1.675 | 1.672 | 1.700 |
| $\mu$, cm$^{-1}$ | 1.71 | 12.47 | 12.68 |
| diffraction meas | | | |
| wavelength $\lambda$, Å | 0.8308 | 0.710 69 | 0.710 69 |
| (sin $\theta/\lambda$ limit, Å$^{-1}$ | 0.8132 | 0.7035 | 0.7035 |
| scan type | $\theta-2\theta$ | $\theta-2\theta$ | $\theta-2\theta$ |
| no. of reflcns | | | |
| tot. | 989 | 1057 | 1231 |
| indept ($R_{int}$) | 380 (0.028) | 619 (0.024) | 617 (0.016) |
| used in refint ($n$) | 320 ($F > 4\sigma(F)$) | 616 ($F > 2\sigma(F)$) | 615 ($F > 2\sigma(F)$) |
| abs cor | Gaussian int. | sphere | sphere |
| transm factors | 0.46−0.56 | 0.69−0.70 | 0.69−0.70 |
| refinement | | | |
| no. of variables ($v$) | 46 | 35 | 35 |
| extinction parameter ($g$) | 0.244(14) | 0.164(6) | 0.09(3) |
| weights $[\sigma^2(F) + xF^2]^{-1}$ | $x = 0.0002$ | $x = 0.0002$ | $x = 0.0001$ |
| $R^a$ | 0.020 | 0.018 | 0.009 |
| $R_w{}^b$ | 0.020 | 0.021 | 0.013 |
| $S$ | 0.80 | 1.19 | 1.09 |

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

crystals of KF·$2H_2O$ with dimensions between 5 and 50 mm were obtained starting with solutions of 62 g of KF in 60 mL of $H_2O$ that were slowly evaporated for several days at about 35 °C over solid KOH as desiccant. The crystals were isolated from the viscous mother liquor, thoroughly dried between filtration paper, and stored in closed vials at room temperature. An analogous procedure was used for (partially) deuterated samples. In the case of completely deuterated crystals, i.e. KF·$2D_2O$, it was found that after several weeks of storage these crystals had decomposed by dehydration to KF, in contrast to KF·$2H_2O$ crystals which did not decompose under the same storage conditions. Due to the instability of the deuterated samples the neutron diffraction work could only be carried out with crystals of KF·$2H_2O$.

**Neutron and X-ray Diffraction.** Single-crystal neutron diffraction work was carried out at the research reactor ORPHEE, Laboratoire Leon Brillouin, Saclay, France, using a P110 four-circle diffractometer with a Cu(220) monochromator and a nominal wavelength of 0.8308 Å ($2\theta_M = 38.40°$). Two crystals were pretreated with liquid nitrogen in order to reduce extinction effects whereby the intensities of some strong test reflections significantly increased (up to three times). Crystal 1, a block of 4.6 × 4.8 × 5.2 mm coated with epoxy resin, served to measure the intensities of 456 reflections at room temperature, whereupon the crystal liquefied and had to be replaced. Crystal 2, an ovaloid of about 3.8 × 3.8 × 6 mm, was subsequently used to complete data collection by measuring additional 533 reflections. The data limit for both crystals was $(\sin\theta)/\lambda \le 0.8132$ Å$^{-1}$. Data reduction included corrections for the Lorentz effect, crystal and system stability monitored by three reference reflections, and absorption effects by the Gaussian integration method using an empirically estimated linear absorption coefficient of 1.71 cm$^{-1}$. These two data sets were then put on the same scale and were merged to 380 independent reflections $[(+h,+k,+l)$; Friedel pairs merged owing to the lack of anomalous dispersion effects in the case of neutron diffraction]. Structure refinement was started with the results of the X-ray diffraction work described below. Anisotropic temperature factors were used for all atoms including hydrogen. The program SHELX76[11] was used to refine the structure. The refinement was based on $F$ and applied weights $w = 1/(\sigma^2(F_o) + 0.0001\ F_o{}^2)$ which gave a satisfactory distribution of weighted structure factor differences. A total of 46 parameters including a single scale factor and an isotropic correction for extinction were varied until shifts were vanishingly small.

X-ray work at 298 and at 120 K was carried out with a Philips PW1100 four-circle diffractometer using graphite monochromatized Mo K$\alpha$ radiation and a Leybold-Heraeus NCD-2 gas stream cooling device. A crystal of KF·$2H_2O$, shaped to a sphere of 0.45 mm diameter and coated with epoxy resin, was used. Accurate cell dimensions were derived from $\pm\theta$ scans of 42 reflections. Reflection intensities were measured by $\theta-2\theta$ scans using a scan range of $1.2 + 0.33 \tan\theta$ (deg), a scan speed of 0.0333° s$^{-1}$, and background times of 10 s on both sides of each scan. The data were corrected for LP, absorption (sphere, $\mu R = 0.25$), and system instability. They were then merged taking into account the inequivalence of Friedel pair reflections (polar space group, significant anomalous dispersion effects). Structure refinement with the SHELX76 program started with the atomic parameters of ref 5 other than hydrogen and allowed for anisotropic temperature factors. Hydrogen atoms were located by difference Fourier maps and were included in subsequent refinements, with a common isotropic temperature factor for each measurement temperature. In the final refinements, 35 parameters including a scale factor and a correction for extinction were varied. The polarity of the reflection data in relation to that of the structure was checked and found to require no change because $R$ values for opposite polarity were approximately 1.1 times larger. Salient experimental data and results of neutron diffraction and X-ray diffraction are summarized in Table 1 and final atomic parameters are given in Table 2.

**Vibrational Spectroscopy.** Infrared spectra were recorded on a Perkin-Elmer Model 1740 FTIR spectrometer, Raman spectra on a PC controlled Jarrell-Ash Model 25−300 spectrometer using the 15454 cm$^{-1}$ exciting line of a Kr ion laser. For low temperature measurements (75 K) an Oxford Instruments CF100 cryogenic unit equipped with a VTC temperature controller was used. Infrared spectra were obtained from fluorocarbon and hydrocarbon mulls sandwiched between $BaF_2$ plates; unpolarized Raman spectra were directly obtained from polycrystalline material. Samples with different degrees of deuteration

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[11] Sheldrick, G. M. SHELX76: program for crystal structure determination. University of Cambridge, England, 1976.

**Table 2.** Atomic Coordinates and Thermal Displacement Parameters (Å$^2$ × $10^4$) for $KF\cdot 2H_2O$, where for Each Atom the First Line Is from Neutron Data at 295 K, While the Second and Third Lines Are from X-ray Diffraction Data at 298 and 120 K, respectively[a]

| atom | $x$ | $y$ | $z$ | $U_{iso}/U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| K | 0.50000 | 0.3879(3) | 0.00000 | 263(7) | 258(7) | 314(8) | 0 | 0 | 20(6) |
| | 0.50000 | 0.38840(4) | 0.00000 | 277(1) | 283(1) | 328(1) | 0 | 0 | 34(2) |
| | 0.50000 | 0.38995(2) | 0.00000 | 109(1) | 107(1) | 119(1) | 0 | 0 | 8(1) |
| F | 0.00000 | 0.0969(2) | 0.1093(2) | 302(5) | 301(5) | 301(5) | 0 | 0 | 19(4) |
| | 0.00000 | 0.0973(2) | 0.1094(1) | 308(4) | 330(4) | 315(4) | 0 | 0 | 16(4) |
| | 0.00000 | 0.0979(1) | 0.1090(1) | 127(3) | 129(2) | 121(2) | 0 | 0 | 5(2) |
| O(1) | 0.50000 | 0.2032(3) | 0.7110(3) | 346(7) | 333(6) | 368(7) | 0 | 0 | −65(5) |
| | 0.50000 | 0.2039(2) | 0.7109(2) | 348(6) | 363(6) | 387(6) | 0 | 0 | −56(5) |
| | 0.50000 | 0.2040(1) | 0.7107(1) | 132(3) | 147(3) | 155(3) | 0 | 0 | −27(2) |
| O(2) | 0.00000 | 0.2918(3) | 0.3969(3) | 425(6) | 304(5) | 311(7) | 0 | 0 | −46(5) |
| | 0.00000 | 0.2925(2) | 0.3968(2) | 452(6) | 331(5) | 323(5) | 0 | 0 | −36(5) |
| | 0.00000 | 0.2923(1) | 0.3970(1) | 183(3) | 129(2) | 120(3) | 0 | 0 | −7(2) |
| H(1) | 0.3127(4) | 0.1003(3) | 0.6804(3) | 393(6) | 459(7) | 502(7) | −27(6) | 4(6) | −28(6) |
| | 0.333(6) | 0.112(3) | 0.684(3) | 592(57) | | | | | |
| | 0.334(4) | 0.117(2) | 0.687(2) | 326(30) | | | | | |
| H(2) | 0.00000 | 0.2268(4) | 0.2938(3) | 501(10) | 486(11) | 372(11) | 0 | 0 | −59(9) |
| | 0.0000 | 0.235(5) | 0.315(4) | 547(69) | | | | | |
| | 0.0000 | 0.232(3) | 0.310(2) | 298(36) | | | | | |
| H(3) | 0.00000 | 0.1414(4) | 0.4616(3) | 528(10) | 417(11) | 423(10) | 0 | 0 | −4(9) |
| | 0.0000 | 0.145(5) | 0.448(3) | 536(81) | | | | | |
| | 0.0000 | 0.148(3) | 0.447(2) | 272(41) | | | | | |

[a] $ATF = \exp[-2\pi^2(h^2U_{11}a^{*2} + ... + 2hkU_{12}a^*b^*)]$.

($H_2O$:$D_2O$ = 100:0 to 80:20 wt %) were investigated to reliably distinguish between the $\bar{\nu}$(OD) stretching frequencies of isotopically dilute HOD and those of $D_2O$ molecules.

**Computational Details.** The electronic structure of solids can be described within density functional theory for treating exchange and correlation effects using the local density approximation (LDA)[12] with the parameters given by Hedin and Lundqvist.[13] For these energy band calculations the linearized augmented plane wave (LAPW) method as embodied in the WIEN93 code[8] was used, a method that is among the most accurate schemes presently available. It is an ab initio scheme since only the atomic numbers of the constituent atoms are required. In the present study the energy band structure was determined using the structural data from the neutron diffraction experiments. Such calculations can now be done on modern workstations within days for one geometry.

The LAPW code is a full-potential method (without any shape approximations), in which the unit cell is partitioned into two types of regions, namely the atomic spheres (with radius $R_{MT}$) and the interstitial region.[8] Inside the atomic spheres atomic-like basis functions are used to describe the wave functions, while plane waves represent the crystalline wave functions in the interstitial region. Potential and charge density were expressed in lattice harmonics (up to $L = 4$) inside the spheres and as a Fourier series in the interstitial region.

In the present calculations a cut-off parameter $R_{MT}|\mathbf{k} + \mathbf{K}_{max}| = 2.75$ was used, where $R_{MT}$ corresponds to the smallest muffin-tin radius (muffin-tin radii are 2.2, 2.2, 0.94, and 0.612 au for K, F, O, and H, respectively) resulting in about 1500 plane waves. The K 3p, K 4s, F 2p, O 2p and H 1s states were treated as valence states, with the K 3s, F 2s, and O 2s states treated as semicore band states using a separate energy window, while all lower states were treated as thawed (**k**-independent) atomic core states. In the irreducible wedge of the Brillouin zone 8 (2) **k**-points were used for the valence (semicore) states in the self-consistency cycle.

## Results and Discussion

**Crystal Structure.** $KF\cdot 2H_2O$ possesses a simple but unique structure.[5,14] Potassium is coordinated by four $H_2O$ and two F moieties in the form of a strongly distorted octahedron in which the F's adopt a *cis*-position (Figure 1). Fluorine exhibits an analogous and also strongly distorted octahedral coordination figure $F(H_2O)_4K_2$ with two K ions in *cis*-position. The two independent water molecules, $H_2O(1)$ and $H_2O(2)$, display distorted tetrahedral coordination. Each of them is bonded to two K ions and donates hydrogen bonds to two F ions. The architecture of the structure (Figure 1) can be described on the basis of $K(H_2O)_4F_2$ octahedra that are mutually linked via shared edges [F + $H_2O(2)$] parallel to the $x$-axis, and via shared vertices [$H_2O(1)$] parallel to the $z$-axis. Corrugated octahedral layers of the composition $KF\cdot 2H_2O$ are thus formed parallel to (010). These layers are reinforced by the intralayer hydrogen bonds O(2)−H(2)···F. The layers are stacked one above the other by translation along the $y$-axis and are mutually linked via the interlayer hydrogen bonds O(1)−H(1)···F and O(2)−H(3)···F.

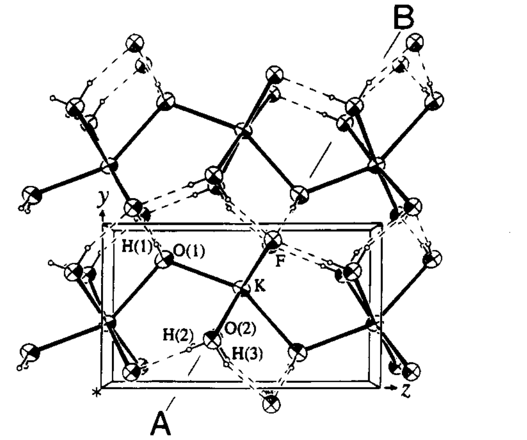

**Figure 1.** Structure of $KF\cdot 2H_2O$ in a perspective view along $x$ (ORTEP plot, 30% ellipsoids, H atoms as small circles). Letters A and B mark the trace of the plane for which the calculated electron densities are shown in Figures 4 and 6.

The K−F and K−O bond lengths in $KF\cdot 2H_2O$ (Table 3) correspond closely to values expected from the ionic radii, according to Prewitt & Shannon:[15] K−F = 2.71 Å, K−O = 2.78 Å. These values may be compared to those of anhydrous KF which exhibits a $KF_6$ octahedron with a distinctly shorter K−F bond length of 2.674 Å, and with those of $KF\cdot 4H_2O$,[16,17]

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[12] Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136B*, 864. Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.
[13] Hedin, L.; Lundqvist, B. I. *J. Phys.* **1971**, *C4*, 2064.
[14] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, England **1984**.
[15] Prewitt, C. T.; Shannon, R. D. *Acta Crystallogr.* **1969**, *B25*, 925.
[16] Beurskens, G.; Jeffrey, G. A. *J. Chem. Phys.* **1964**, *41*, 917.
[17] Zottl, M.: Thesis, Technical University of Vienna, 1993.

**Table 3.** Selected Bond Lengths (Å) for the Coordination Figures in $KF{\cdot}2H_2O$, Where Neutron Diffraction Values Were Calculated with the X-ray Unit Cell Dimensions at 298 K[a]

| | | | X-ray diffr | |
|---|---|---|---|---|
| | | neutron diffr 295 K | 298 K | 120 K |
| K | $-F^{i,ii}$ | 2.176(2) | 2.716(1) | 2.703(1) |
| K | $-0(1^{iii})$ | 2.726(2) | 2.727(1) | 2.714(1) |
| K | $-0(1^{iv})$ | 2.822(2) | 2.817(1) | 2.794(1) |
| K | $-0(2^{iv,v})$ | 2.784(2) | 2.781(1) | 2.762(1) |
| F | $-K^{i,vi}$ | 2.716(2) | 2.716(1) | 2.703(1) |
| F | $-0(1^{vii,viii})$ | 2.719(2) | 2.722(1) | 2.711(1) |
| F | $-0(2^{i})$ | 2.734(3) | 2.733(2) | 2.720(1) |
| F | $-0(2^{vii})$ | 2.753(3) | 2.758(1) | 2.741(1) |
| O(1) | $-K^{ix}$ | 2.726(2) | 2.727(1) | 2.714(1) |
| O(1) | $-K^{x}$ | 2.822(2) | 2.817(1) | 2.794(1) |
| O(1) | $-F^{xi,xii}$ | 2.719(2) | 2.722(1) | 2.711(1) |
| O(2) | $-K^{x,xiii}$ | 2.784(2) | 2.781(1) | 2.762(1) |
| O(2) | $-F^{i}$ | 2.734(3) | 2.733(2) | 2.720(1) |
| O(2) | $-F^{xi}$ | 2.753(3) | 2.758(2) | 2.741(1) |

[a] Symmetry code: none or (i) $x, y, z$; (ii) $1 + x, y, z$; (iii) $x, y, -1 + z$; (iv) $x, 1 - y, -{}^1/_2 + z$; (v) $1 + x, 1 - y, -{}^1/_2 + z$; (vi) $-1 + x, y, z$; (vii) $x, -y, -{}^1/_2 + z$; (viii) $-1 + x, -y, -{}^1/_2 + z$; (ix) $x, y, 1 + z$; (x) $x, 1 - y, {}^1/_2 + z$; (xi) $x, -y, {}^1/_2 + z$; (xii) $1 + x, -y, {}^1/_2 + z$; (xiii) $-1 + x, 1 - y, {}^1/_2 + z$.

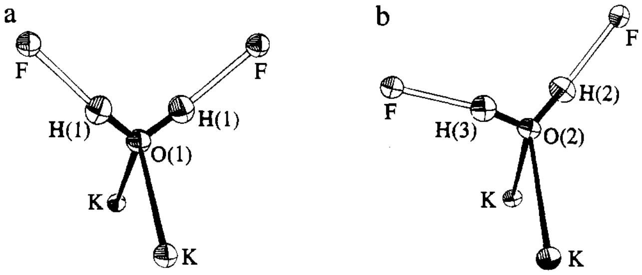

**Figure 2.** Coordination and hydrogen bonding of the two independent water molecules in $KF{\cdot}2H_2O$ (ORTEP plot, 30% ellipsoids). Both water molecules are located on crystallographic mirror planes defined by the atoms K-O(1)-K (a) and F-O(2)-F (b).

which contains a $K(H_2O)_6$ octahedron with a mean K−O distance of 2.766 Å.[17] The coordination of the water molecules in $KF{\cdot}2H_2O$ and the geometry of the hydrogen bonds formed by them is visualized in Figure 2 and numerical data are given in Table 4. The tetrahedral coordination of $H_2O(1)$ is most asymmetric with respect to the positions of the two K atoms (Figure 2a). In contrast, the coordination of $H_2O(2)$ is most asymmetric with respect to the positions of its hydrogen bond acceptors, and this molecule adopts a "skew" orientation (Figure 2b) which can be regarded as a compromise within the frame of four ligands, i.e. two K and two F. In $KF{\cdot}2H_2O$ there are only three crystallographically different O−H··F type hydrogen bonds. They are essentially straight in their O−H··F angles (≥ 170°) and show O··F distances in the range of 2.72−2.76 Å. O··F distances between 2.563 and 2.906 Å, with a mean value of 2.674 Å, have been reported[18] in an analysis of crystalline hydrates with O−H··F bonds studied by neutron diffraction. Similar situations were found in related work based on X-ray as well as neutron diffraction data.[17,19,20] In the title compound and in $KF{\cdot}4H_2O$ (O··F = 2.71−2.78 Å[16,17]) the lengths of the O−H··F hydrogen bonds can be well explained by the relatively low K−O bond valence sums[21] of each water molecule (including some O−H··O for $KF{\cdot}4H_2O$) . If the cation−oxygen bond valences for a water molecules are larger than those in $KF{\cdot}2H_2O$, then distinctly shorter O−H··F bonds are observed: e.g. in $CuF_2{\cdot}2H_2O$ (O··F = 2.64 Å)[22] and in $ZnF_2{\cdot}4H_2O$ (mean O··F = 2.62 Å for four short bonds).[2,17]

The present study confirms the earlier reported crystal structure with a significant increase in accuracy. The agreement between the present room temperature neutron and X-ray structures is good with respect to non-hydrogen atom positions which differ only by ≤0.004(2) Å. The shift of hydrogen atom positions determined by X-ray diffraction along the O−H bond vectors toward the oxygen atoms leads to O−H distances of 0.78−0.89 Å that are shorter than the true O−H distances found by neutron diffraction (H nucleus to O nucleus distances of 0.966−0.971 Å for $KF{\cdot}2H_2O$). As to the thermal vibration parameters those of the neutron diffraction are consistently larger by 0.0016 $Å^2$ (in terms of $U$ values) for the neutron than for the X-ray diffraction, an effect commonly encountered in combined diffractional studies.

Comparison of the X-ray structures at 298 and 120 K reveals relatively isotropic temperature effects. When the compound is cooled down to 120 K, the unit cell edges shrink by 0.52% for $a$ and $b$, and by 0.60% for $c$. Simultaneously the atomic thermal vibration parameters are more than halved. In terms of atomic positions the largest shift between 298 and 120 K is observed for K [0.008(1) Å], while those of F and O are only between 0.001 and 0.005 Å. Thus when the compound is cooled from 298 to 120 K, a relatively small and homogeneous decrease in all bond lengths including hydrogen bonds is observed. These results are in agreement with essentially isotropic bond connections, in contrast to many other salt hydrates, e.g. $Sr(SCN)_2{\cdot}3H_2O$,[23] where hydrogen bonds show larger temperature effects than bonds to cations.

**Vibrational Spectra.** Three uncoupled $\bar{\nu}$(OD) stretching frequencies, 2462, 2478 and 2491 $cm^{-1}$, were observed in the low temperature (75 K) spectra of partially deuterated samples (Figure 3), which agrees well with the structural data of the title compound: the number of $\bar{\nu}$(OD) frequencies equals the number of crystallographically nonequivalent O−H(D)··F groups, and additionally, the rather small differences between the frequencies agree with the equally small differences between the hydrogen bond geometries, in particular between the hydrogen bond distances. Assuming a monotonic relationship between $\bar{\nu}$(OD) frequencies and O··F (or H··F) bond distances (Table 4), these frequencies can reasonably well be assigned to the groups O(1)−H(D)(1)··F, O(2)−H(D)(2)··F, and O(2)−H(D)(3)··F, respectively. Although such assignments are common when dealing with hydrogen bonding in hydrates, they may be questioned, since experimental frequency−distance correlations are known to be more or less widely scattered. It has been shown, however,[1,24] that the amount of scatter is largely determined by differences in the proton acceptors but to a minor extent by different lone pair coordinations of the water molecules or by deviations from linearity. In the title compound the two water molecules are very similar with respect to both the proton acceptors (two F ions) and the lone pair coordinations (two K ions at similar average distances), so that we have strong confidence that the assignments are correct. Additional evidence for this view comes from the theoretical calculations (see section below).

Figure 3 shows a graph of uncoupled $\bar{\nu}$(OD) frequencies (IR values at 75 K) versus O··F bond distances (X-ray determined at 120 K) of the O−H··F hydrogen bonds in $KF{\cdot}2H_2O$ and in

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(18) Chiari, G.; Ferraris, G. *Acta Crystallogr.* **1982**, *B38*, 2331.
(19) Simonov, V. I.; Bukvetskii, B. V. *Acta Crystallogr.* **1978**, *B34*, 355.
(20) Massa, W.; Babel, D. *Chem. Rev.* **1988**, *88*, 275.
(21) Brown, I. D. *Acta Crystallogr.* **1977**, *B33*, 1305. Brese, N. E.; O'Keefe, M. *Acta Crystallogr.* **1991**, *B47*, 192.
(22) Prince, E. *J. Chem. Phys.* **1972**, *56*, 4352.
(23) Mereiter, K.; Preisinger, A. *Acta Crystallogr.* **1992**, *C48*, 1367.
(24) Mikenda, W.; Mereiter, K.; Preisinger, A. *Inorg. Chim. Acta* **1989**, *161*, 21.

**Table 4.** Hydrogen Bond Distances (Å) and Angles (deg) for KF·2H₂O, Where for Each Atom the First Line Is from Neutron Data at 295 K, While the Second and Third Lines Are from X-ray Diffraction Data at 298 and 120 K, Respectively

| O−H···A | O−H | H−A | O−A | H−O−H′ | O−H−A | A−O−A′ |
|---|---|---|---|---|---|---|
| O(1)−H(1)···F | 0.971(2) | 1.752(2) | 2.719(2) | 103.9(2) | 174.0(2) | 97.3(1) |
| | 0.86(2) | 1.86(2) | 2.722(1) | 104(2) | 174(2) | 97.2(1) |
| | 0.84(1) | 1.88(1) | 2.711(1) | 108(1) | 171(1) | 97.1(1) |
| O(2)−H(2)···F | 0.971(4) | 1.764(3) | 2.734(3) | 105.9(2) | 177.9(2) | 111.2(1) |
| | 0.78(3) | 1.96(3) | 2.733(2) | 98(3) | 179(3) | 111.2(1) |
| | 0.82(2) | 1.90(2) | 2.720(1) | 99(2) | 179(2) | 111.1(1) |
| O(2)−H(3)···F | 0.966(3) | 1.796(3) | 2.753(2) | | 169.6(3) | |
| | 0.89(3) | 1.90(3) | 2.758(2) | | 162(2) | |
| | 0.87(2) | 1.90(2) | 2.741(1) | | 163(2) | |

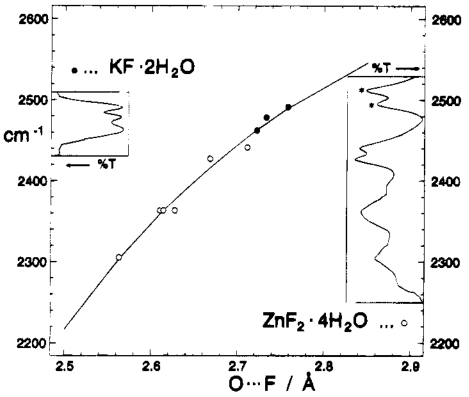

**Figure 3.** Correlation between uncoupled $\bar{\nu}$(OD) frequencies and O···F distances for KF·2H₂O (dots) and ZnF₂·2H₂O (circles). The inserts show 75 K IR spectra of partially deuterated samples [range of $\bar{\nu}$(OD) stretching vibrations; bands arising from O−D···O groups are indicated by asterisks].

ZnF₂·4H₂O; the regression curve was calculated for a $\bar{\nu}(\mathrm{OD}) = 2727 - A \times \exp\{-B(\mathrm{O}\cdots\mathrm{F})\}$ type function,[1,7] for which $A = 1.378 \times 10^6$ and $B = 3.15$ resulted. Although good quality structural and spectroscopic data are available in the literature for ZnF₂·4H₂O,[2,4] we used our data for the correlation plot to ensure maximum comparability with the data of the title compounds. Our 75 K $\bar{\nu}$(OD) frequencies are almost identical with the 100 K literature values, except that we did not consider two weak shoulders as distinct $\bar{\nu}$(OD) absorption bands (Figure 3); our O···F distances, which are taken from a recent X-ray refinement at 120 K,[3,17] are slightly different (0.015 Å on average) from those of the room temperature neutron diffraction study reported in literature.[2] Figure 3 is significant for several reasons. First, the data of the title compound extend a previously published correlation which was based on the data of the zinc compound only.[4] Second, not necessarily expected, excellent consistency is found among the data of the two compounds: the experimental points of potassium fluoride fit almost perfectly to the regression curve calculated from the points of the zinc compound. Finally, the scatter of points within the plot (with a correlation coefficient of 0.989) is remarkable small which results from the fact, that data are restricted to simple fluoride anions acting as proton acceptors, in contrast to complex fluorides such as $\mathrm{SiF_6}^{2-}$. An extended frequency−distance correlation of O−H···F hydrogen bonds which includes a number of complex fluoride hydrates is given elsewhere.[25]

Except of the uncoupled $\bar{\nu}$(OD) frequencies the vibrational spectra do not provide much essential information. Besides some Raman determined low frequency lattice modes which can not be reliably assigned, only the well-known broad band features of water spectra are observed: a stretching band at 3350 cm⁻¹, a deformational band with two submaxima at 1695 and 1730 cm⁻¹, and librational bands at 750 cm⁻¹ (IR) and 570 cm⁻¹ (Raman). The only noticeable point concerns the two water bending frequencies, which differ by as much as 35 cm⁻¹. Water bending frequencies are known to be determined to a comparable amount by the hydrogen bonds and by the lone pair coordinations.[26] From the similar hydrogen bond distances and K−O distances of the two water molecules one would expect the bending frequencies to differ by not more than about 10 cm⁻¹. A possible reason for the observed 35 cm⁻¹ difference may be found in the apparently different distortions of the coordination polyhedra of the two water molecules, as discussed in the previous section on the crystal structure, and the associated potassium hydrogen repulsion effects.

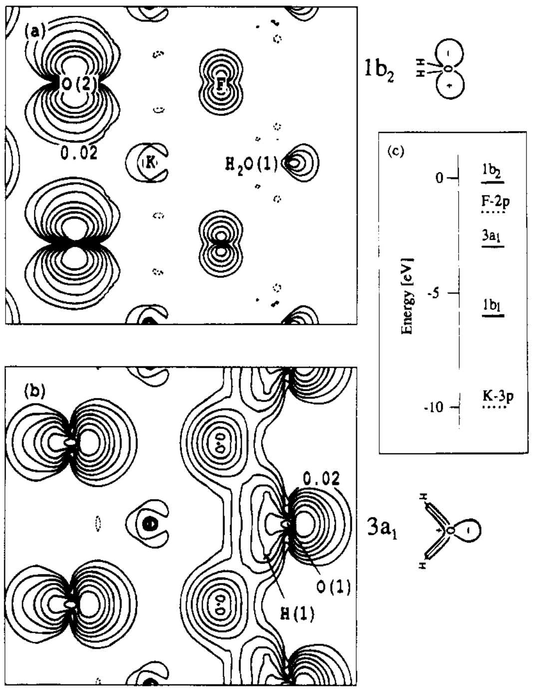

**Figure 4.** (a, b) Electron densities in a plane indicated in Figure 1 by A/B of (a) 1b₂ and (b) 3a₁ states with contour values from 0.02 to 2.56 e Å⁻³ (in multiples of 2). (c) Schematic MO diagram.

**Energy Band Structure and Electron Densities.** From calculations of the free water molecule it is known that the molecular orbital (MO) scheme (Figure 4c) consists of the following occupied states (with increasing energy): $2a_1 < 1b_1 < 3a_1 < 1b_2$. The 2a₁, 1b₁, and 3a₁ states are bonding in character and are linear combinations of the H 1s orbital with the O 2s and 2p orbitals, while the 1b₂ state corresponds to the noninteracting lone pair at the oxygen atom. The corresponding states in KF·2H₂O form narrow energy bands at −20 eV (2a₁), −6 eV (1b₁), −3 eV (3a₁) and −0.2 eV (1b₂) with respect to

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(25) Mikenda, W.; Steinböck, S. *J. Mol. Struct.*, in press.

(26) Falk, M. *Spectrochim. Acta*, **1984**, *43A*, 43.

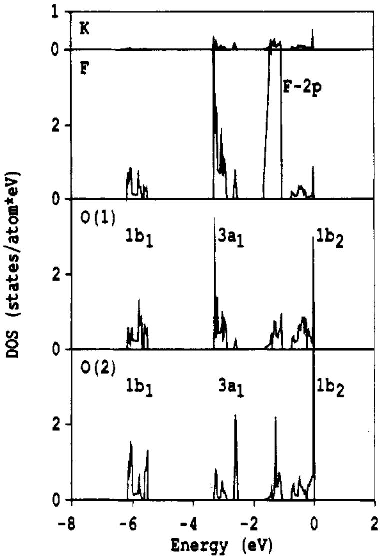

**Figure 5.** Partial density of states (DOS) of $KF{\cdot}2H_2O$ corresponding to the atomic spheres K, F, O(1), and O(2), respectively. The peaks are labeled according to the MO scheme (see Figure 4c).

the Fermi energy ($E_F$) with a width of about 0.5 eV (Figure 5). The F 2p (K 3p) states were obtained at −1.5 eV (−10 eV) and are very narrow with a width less than 0.6 eV (0.2 eV). The related density of states (DOS) can be decomposed into partial contributions (Figure 5) using the respective charge inside the atomic spheres as weight. Since the H sphere is very small, the water MOs are best represented by the respective O DOS. The $H_2O(2)$ water molecule has two different O−H distances, namely O(2)−H(2) and O(2)−H(3), and thus the O(2) partial DOS shows a splitting of the $1b_1$ and $3a_1$ states with a double peak structure. The O(1) partial DOS corresponding to the symmetric water molecule $H_2O(1)$ remains unsplit, similar to the nonbonding $1b_2$ peak.

The K DOS is a very small component indicating a mostly ionic interaction with hardly any covalent contribution (Figure 5). The F DOS shows a significant (covalent) contribution to the $3a_1$ $H_2O$ states (Figure 5), while for the $1b_1$ state the interaction is much smaller, since it is lower in energy and thus more localized. The F admixture to the $1b_2$ state (O lone pair) is rather small. Note that the large F-sphere contains practically all F-like contributions whereas the small O-sphere (required because of the small O−H distance) includes only about 30%.

In order to analyze the hydrogen bonds in more detail, the corresponding electron densities of the two most significant ($3a_1$ and $1b_2$) states are shown in the plane as indicated in Figure 1 by labels A and B. This plane contains a K (near the center of Figure 4 and 6), two F, two O(2) of the $H_2O(2)$ and finally one $H_2O(1)$ of the next unit cell. Note that $H_2O(1)$ lies in this plane with the H pointing toward F, while $H_2O(2)$ is oriented perpendicular to the plane so that its two H are above and below the plane and the oxygen lone pair is in the plane. Figure 4a and 4b shows two states, $1b_2$ and $3a_1$, which can be compared with the respective schematic electron density of a free water molecule (as sketched in Figure 4). From the similarity in shape these two band states correspond to the $3a_1$ and $1b_2$ orbitals of the free molecule. The $1b_2$ state (Figure 4a) can be seen for $H_2O(2)$ and shows mainly density contributions from the O(2) lone pair and hardly any charge build-up toward K, indicating that the interaction between this water molecule and the K ion is mostly electrostatic. This observation is consistent with the partial DOS described above (Figure 5) which has no significant contribution from K to the $1b_2$ state. The $3a_1$ state (Figure 4b), however, is visible at $H_2O(1)$ and shows a clear interaction between H and F with a fluorine-contribution to both the electron density (Figure 4b) and the DOS (of about 20%).

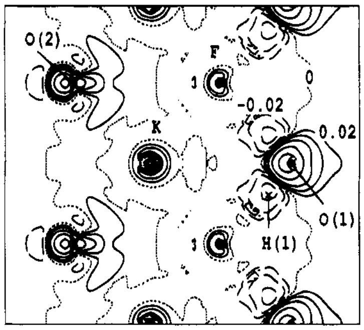

**Figure 6.** Difference in electron density distribution between that of $KF{\cdot}2H_2O$ and the reference system of free ions $K^+$, $F^-$ and $H_2O$ for the plane indicated in Figure 1 by A/B. Contour values in steps of ±0.02 e Å$^{-3}$.

**Table 5.** Experimental and Calculated O−H and H···F Distances (Å)

| water 1: H(1)−O(1)−H(1) | exptl | LAPW | water 2: H(2)−O(2)−H(3) | exptl | LAPW |
|---|---|---|---|---|---|
| O(1)−H(1) | 0.971 | 1.031 | O(2)−H(2) | 0.971 | 1.034 |
| | | | O(2)−H(3) | 0.966 | 1.026 |
| H(1)···F | 1.752 | 1.678 | H(2)···F | 1.764 | 1.684 |
| | | | H(3)···F | 1.796 | 1.722 |

To investigate the F···$H_2O(1)$ interaction a reference calculation was done, in which the water molecules were kept at their respective positions, but the K and F ions were removed from the unit cell, yielding an electron density of the water molecules in the crystal geometry. Figure 6 displays the density difference $\Delta\varrho$ between the title compound and this reference system (plus the free ions) showing directly the influence of the K and F ions on the water molecules. There is a negative $\Delta\varrho$ at the H(1) positions and a positive $\Delta\varrho$ at O(1); thus, the F ion weakens the O−H bond and leads to a charge transfer from H to the oxygen lone pair region. For the $H_2O(2)$ molecule, which has its lone pair orbital in the plane shown in Figure 6, a weak splitting of this lone pair region appears with two diffuse maxima at about 1Å (at about one-third) along the line connecting the O(2) with the K nuclei. A similar effect on the lone pairs has been observed experimentally in other hydrates.[27] In summary, the interaction of $H_2O$ with K is mostly electrostatic, while that with F has an additional covalent contribution or at least a polarization effect of about 20%.

In our present version of the LAPW method we can determine structural parameters or atomic positions by minimizing the corresponding total energy $E_{tot}$. Since such calculations must be carried out for each atomic configuration separately, only the O−H distances were optimized because of the substantial computational effort. For $H_2O(1)$ we moved the H(1) along the O(1)−H(1) axis keeping the $H_2O(1)$ angle fixed at the values obtained by neutron diffraction. In this case both H(1) atoms are moved according to a symmetric stretching vibration keeping the mirror plane perpendicular to the $H_2O(1)$. For $H_2O(2)$ we moved both hydrogen atoms, H(2) and H(3) independently, for example, keeping O(2)−H(2) fixed and varying O(2)−H(3) or vice versa, where the $H_2O(2)$ angle remains fixed.

The calculated O−H distances are listed in Table 5 where one can see that the O−H distances are about 6% too long with respect to the neutron diffraction data. It is known from previous work that LDA calculations often underestimate lattice constants, e.g. in metals by up to 3%, but overestimate weak

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(27) McIntyre, G. J.; Ptasiewicz-Bak, H.; Olovsson, I. *Acta Crystallogr.* **1990**, *B46*, 27.

interactions. For example, in the molecular crystals such as $Br_2$ and $Cl_2$ the nearest neighbor distance is too long while the next nearest neighbor distance is too short.[28] In spite of these well-known deficiencies of LDA calculations, at least the trend in O−H distances agrees with the experiment; e.g., O(2)−H(2) is found to be larger than O(2)−H(3). In order to check the convergence we increased the cutoff parameter $R_{\mathrm{MT}}|\mathbf{k} + \mathbf{K}_{\max}|$ from 2.75 to 3 and obtained an O−H distance that was 0.5% smaller than the original value, indicating that a larger basis set would be desirable.

Using a simple harmonic oscillator fit to the total energy as a function of the H(2) position [along O(2)−H(2)···F] or the H(3) position [along O(2)−H(3)···F], vibrationally uncoupled $\tilde{\nu}$(OH) frequencies were calculated for the $H_2O(2)$ molecule. $\tilde{\nu}$(OH) and $\tilde{\nu}$(OD) were found to be slightly lower, by about 1%, for O(2)−H(2) than for O(2)−H(3), which is consistent with the differences between the corresponding O−H···F bond distances, O(2)−H(2)···F < O(2)−H(3)···F, and also agrees with the (equally) small differences between the experimentally determined $\tilde{\nu}$(OD) frequencies of isotopically dilute HOD molecules, 2478 and 2491 $cm^{-1}$. The absolute $\tilde{\nu}$(OD) values, however, are substantially higher (3140 and 3179 $cm^{-1}$) and are quite sensitive to basis set convergence. Due to the high computational effort, however, it was not possible to further increase the cutoff parameter.

## Summary

This is the first investigation in which crystallographic, vibrational spectroscopic experiments and quantum mechanical calculations were combined to obtain information on hydrogen bonding in hydrates. Accurate structural data, in particular the positions of the H atoms, are necessary, because the interpretation of the vibrational spectra rely on well-determined distances. The electron density calculations provide direct insight into the chemical bonding. The charge distribution of the hydrate is nearly tetrahedral with a small charge splitting in the lone pair region and shows a strong electrostatic interaction with potassium and an additional covalent contribution in the H···F bond. The present work has led to a consistent picture of the hydrogen bonds in $KF{\cdot}2H_2O$. These promising results suggest that analogous studies should be extended to related systems in order to derive more general conclusions.

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**Supplementary Material Available:** Listings of complete bond distances and angles (11 pages). Ordering information is given on any current masthead page.

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[28] Blaha, P.; Schwarz, K. *J. Mol. Struct. (Theochem)* **1992**, *261*, 335.