An infrared study of the stretching modes of the water molecules in $ZnF_2 \cdot 4H_2O$

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Abstract—The IR spectra of ZnF_2 ·4H₂O and its deuterated analogues are reported at ambient and liquidnitrogen temperatures. The O-H and O-D stretching and bending vibrations of the water molecules are analysed in detail. The two types of water molecules give rise to different absorption peaks in the O-H and O-D stretching regions in samples that contain isotopically dilute HDO groups. The strongly hydrogen-bonded water molecules H₂O(1) and H₂O(4) show four broad O-H and O-D stretching modes at lower frequencies, while the weaker hydrogen-bonded ones H₂O(2) and H₂O(3) give rise to four narrow bands at higher frequencies. The ν_{OD} frequencies of isotopically dilute HDO groups correlate very well with the known R(H---F) and R(H---O) distances in the crystals and the assignment of these modes was done on this basis. It was also found that the ratio ν_{OH}/ν_{OD} decreases with decreasing values of R(H---O) or R(H---F) in ZnF₂·4H₂O.

INTRODUCTION

THE vapour of aqueous HF is highly reactive and reacts with metals to form metal fluoride hydrates [1, 2]. The members of the homologue series $MF_2 \cdot 4H_2O$ (M = Fe, Co, Ni and Zn) are examples of the products of such reactions. They belong to the orthorhombic space group $Pca2_1(C_{2\nu}^5)$ with Z = 4 [3–7]. In this series, only $ZnF_2 \cdot 4H_2O$ has been studied in great detail by means of X-rays [3, 5, 6] and neutron diffraction techniques [4]. In order to throw more light on the structures of the homologue series $MF_2 \cdot 4H_2O$ (M = Fe, Co and Ni), crystals of these compounds have been prepared and characterized by means of Mössbauer spectroscopy, X-ray powder diffraction patterns, electronic spectroscopy, IR spectroscopy and thermochemical methods [7]. However, in the present paper, the results obtained with FT-IR spectroscopy on the well-known compound $ZnF_2 \cdot 4H_2O$ are reported and in a subsequent publication the IR results obtained in a study of the water molecules in the compounds $MF_2 \cdot 4H_2O$ (M = Fe, Co, Ni) will be compared and contrasted [8]. In the latter two studies, the IR spectra of the water molecules at varying degrees of isotopic substitution are reported over a wide range of temperatures.

EXPERIMENTAL

 ZnF_2 ·4H₂O was prepared by dissolving Zn (3 g of 99.5% purity) in hot deoxygenated HF (50 cm³ of a 40% solution) while constantly bubbling nitrogen through the solution to ensure an inert atmosphere. The solution was cooled to room temperature and deoxygenated ethanol was then added, and white crystals of ZnF_2 ·4H₂O precipitated from the solution. The product was filtered, washed with ethanol and then dried at room temperature under a nitrogen atmosphere. The D₂O content of the crystals was varied by the addition of varying amounts of D₂O (99.8%) to the 40% HF. In the case where a high D₂O content was required, the metal fluoride was added to D₂O containing a few drops of HF. The metal and fluorine contents of the samples were determined by chemical methods.

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Atoms	Distance	Atoms	Distance	Atoms	Distance	
Zn-F(1)	2.05	O(1)-O(2)	3.09	O(1)-F(1)	2.87	
Zn-F(2)	2.00	F(1)-O(2)	2.86	F(1)-O(4)	3.02	
Zn-O(1)	2.12	F(2) - O(2)	2.99	O(3)-F(1)	3.91	
Zn - O(2)	2.14	O(4) - O(2)	2.88	O(3) - F(2)	2.84	
Zn - O(3)	2.08	O(4) - F(2)	2.85	O(3) - O(1)	2.95	
Zn-O(4)	2.09	F(2)-O(1)	2.94	O(3)-O(4)	3.01	

Table 1. Interatomic distances in Å of the $ZnF_2 \cdot 4H_2O$ octahedron [4]

The FT-IR spectra were obtained between 4000 and 400 cm⁻¹ and 600 and 200 cm⁻¹, using a Bruker Model 113 V spectrometer. The spectra were recorded of samples dispersed in KBr pellets, or in the form of Nujol mulls on KBr, AgBr or CsI windows. In the case of KBr pellets the samples tend to dehydrate under the pressure required to prepare the pellets and/or to react with the KBr matrix. An evacuated cryostat cooled by means of liquid nitrogen was used for the low-temperature measurements. This cell was designed and constructed in our laboratories.

CRYSTAL STRUCTURES

The general positions of the fluorine, oxygen and hydrogen atoms in $ZnF_2 \cdot 4H_2O$ have been determined [4]. The structure of $ZnF_2 \cdot 4H_2O$ largely consists of rather regular octahedra of four oxygen atoms belonging to the water molecules and two fluorine atoms in a *trans* orientation [4]. These results are evident from the structural data summarized in Table 1. These octahedra are bonded by a system of hydrogen atoms in which all eight hydrogen atoms participate [4]. The structure of this compound is shown in Fig. 1. It is evident from this figure that two types of water molecule occur in the crystals, despite the fact that there are four crystallographically distinct ones in the unit cell. The first type, exemplified by $H_2O(1)$ and $H_2O(4)$, is characterized by the fact that both the hydrogen atoms of the water molecules are hydrogen-bonded to the fluorine atoms (Table 2). In the second type, exemplified by $H_2O(2)$ and $H_2O(3)$, the hydrogen atoms are hydrogenbonded to fluorine and oxygen atoms surround the F(1), F(2), O(1) and O(4) atoms. The O(1)-H(1)-F(2) hydrogen bonds of 2.56 Å are the strongest fluorine-oxygen bonds in



Fig. 1. The crystal structure of ZnF_2 $^{\prime}4H_2O$ as determined by a neutron diffraction study [4] showing the coordination octahedra around the zinc atom. Some of the interatomic distances are given in Å.

Stretching modes of water molecules in ZnF2.4H2O

О-НҮ	0Y	0-H	НҮ	Angle O-H-Y	НН	Angle H-O-H	Angle Y-O-Y
O(1)-H(1)F(2)	2.56	0.95	1.62	173.3	1.56	109.1	106.9
O(1)-H(8)F(1)	2.61	0.96	1.68	160.3			
O(2)-H(5)F(1)	2.67	0.93	1.74	173.0	1.56	109.0	105.1
O(2)-H(6)O(4)	2.92	0.99	1.93	177.8			
O(3)-H(3)F(2)	2.72	0.98	1.75	168.5	1.56	111.4	112.9
O(3)-H(4)O(1)	2.81	0.91	1.90	176.1			
O(4)-H(2)F(2)	2.62	0.99	1.66	164.5	1.59	106.4	96.8
O(4)-H(7)F(1)	2.61	1.00	1.62	174.8			

Table 2. Hydrogen bonds in ZnF₂·4H₂O

the structure. The length of the other fluorine-oxygen bonds and other structural data are summarized in Tables 1 and 2.

The first type of water molecule, $viz H_2O(1)$ and $H_2O(4)$, is characterized by small differences in the O-H bond lengths within the respective water molecules and the site symmetry of these molecules is therefore very close to C_2 . In the second type of water molecule, $viz H_2O(2)$ and $H_2O(3)$, the r(O-H) values differ considerably in the water molecules and the hydrogen bonds formed by these molecules are much weaker than those of the first type.

The strong hydrogen bonds occur in the *bc*-plane of the molecule and the respective $ZnF_2 \cdot 4H_2O$ octahedra are joined in this plane. The strongest hydrogen bonds, *viz* O(1)-H(8)--F(1) and O(4)-H(2)--F(2), occur parallel to the *b*-axis. Short R(H--Y) distances suggest the existence of strong hydrogen bonds. However, a direct correlation could not be obtained in all cases between r(O-H) and R(H--Y) and it therefore appears that crystal packing effects and M-O bond lengths also play a role in determining the length of the O-H bonds.

SELECTION RULES

Under the space group $Pca2_1(C_{2\nu}^5)$ with Z = 4 for MF₂·4H₂O the vibrations of the water molecules should reflect the existence of four crystallographically distinct water molecules. This is so since, with Z = 4, there are 16 water molecules in the unit cell and under the space group $C_{2\nu}^5$ there are only four C_1 sites available that can accommodate a maximum of four molecules. Under $C_{2\nu}$ space group symmetry, each of the fundamental modes for each of the water molecules under $C_{2\nu}$ symmetry for the "free" groups, viz $\nu_1(A_1)$, $\nu_2(A_1)$ and $\nu_3(B_2)$, can theoretically split into $A_1(IR, R) + A_2(R) + B_1(IR, R) + B_2(IR, R)$ components. This means that a total of $12A_1 + 12A_2 + 12B_1 + 12B_2$ vibrational bands can be expected for the internal modes of the water molecules. These results are summarized in Table 3. However, it is unrealistic to expect that all of these components would be resolved in the IR spectra of powdered samples.

Table 3.	Irreducible representations of the	vibrations in the m	ietal fluoride hydrates	$MF_2 \cdot 4H_2O$ (M = Fe, Co.
		Ni, Zn)		

C _{2p} factor group symmetry	MF ₂				<u></u>		
	Acoustic	Lattice modes	Librations	Molecular vibrations	Lattice modes	Librations	Molecular vibrations
$\overline{A_1(IR, R)}$	1	- 3	3	3	12	12	12
$A_2(\mathbf{R})$	1	3	3	3	12	12	12
$B_1(IR, R)$		3	3	3	12	12	12
$B_2(IR, R)$	1	3	3	3	12	12	12



Fig. 2. The mid-IR spectra of ZnF_2 ·4H₂O at 296 K (top) and 100 K (bottom).

Results and Discussion

The mid-IR spectra of ZnF_2 ·4H₂O at ambient and low temperatures are shown in Fig. 2, and those of ZnF_2 ·4H₂O at various degrees of deuteration in Fig. 3. The assignments of the bands shown in these spectra are summarized in Table 4. To summarize very briefly, the stretching modes ν_1 and ν_3 occur above 3000 cm⁻¹, the bending modes ν_2 between 1500 and 1800 cm⁻¹ and the librational modes below 1000 cm⁻¹. In addition to these modes of the water molecules, several Zn-O stretching modes and Zn-F stretching and bending modes were observed in the IR spectra of ZnF_2 ·4H₂O. Generally speaking, however, it is clearly evident in Fig. 2 that the stretching modes are far too broad and ill-defined at room temperature to even attempt an unambiguous assignment of modes. Even the bending mode, ν_2 , which occurs in a frequency range that does not overlap with those of other combination or overtone bands, does not provide any unambiguous evidence about the number of components of this band. More details are evident in Table 4.

It is well known that the frequencies of v_{OH} and v_{OD} in crystal hydrates correlate well with r(O-H), R(H---Y) and R(O---Y) [9-11]. A decrease in the value of r(O-H) and an increase in R(H---Y) and R(O---Y) generally cause increases in the frequencies of v_{OH} and v_{OD} . However, it has been mentioned before that no direct correlation exists between r(O-H) and R(H---F) in ZnF_2 ·4H₂O, making a correlation of these bond lengths and H---F distances with the frequencies of v_{OH} and v_{OD} rather difficult. To assign $v_{OH,OD}$ to a specific O-H---Y group, it is necessary to determine the main contributor to the difference in the $v_{OH,OD}$ frequencies. This difference can be attributed to r(O-H), R(H---Y) or R(O---Y).

It can be noted from Table 2 that four short r(O-H) bond lengths of 0.91-0.96 Å and three longer r(O-H) bond lengths of 0.98-1.00 Å occur in the structure. If $v_{OH,OD}$ are



Fig. 3. The mid-IR spectra of ZnF₂·4H₂O at varying degrees of deuteration at 296 and 100 K. From the top the spectra are shown of ZnF₂·4H₂O (<10% HDO) at 296 and 100 K and of the compound with >80% deuteration at the same temperatures.

assigned using the usual correlation between r(O-H) and $\nu_{OH,OD}$, seven bands consisting of four higher and three lower frequency bands can be expected. Using this assignment, no differentiation can be made between the different water molecules.

A further noteworthy point is that three different R(H--Y) distances were found to occur in $H_2O(1,4)$, and four distinct R(H--Y) distances in $H_2O(2,3)$ (Table 2). If $\nu_{OH,OD}$ are assigned using the expected correlation between R(H--Y) and $\nu_{OH,OD}$, again seven bands consisting of four higher frequency and three lower frequency bands can be expected. Similar results are expected if the correlation between R(O--Y) and $\nu_{OH,OD}$ is used. In the last two cases the bands of each water molecule are situated in a specific frequency region.

From r(O-H), R(H--Y) and R(O--Y) versus $\nu_{OH,OD}$ frequency correlations alone, it is therefore not possible to assign $\nu_{OH,OD}$ unambiguously. Other parameters, such as the band shapes, have to be taken into account. Seven $\nu_{OH,OD}$ modes representing the HDO groups can however be expected to occur in the IR spectra of isotopically dilute HDO groups in the $ZnF_2 \cdot 4H_2O$ lattice. The assignment of ν_{OD} was further investigated by plotting ν_{OD} against r(O-H), R(O--Y) and R(H--Y) using the expected correlations. The graph of ν_{OD} versus r(O-H) follows a smooth curve with a negative slope, as can be seen in Fig. 5(a). This graph, however, is difficult to explain in terms of the crystal structure of $ZnF_2 \cdot 4H_2O$. The four broad absorption bands indicate a similar crystallographic environment for the four longer O-H bonds. The four sharper bands indicate another crystallographic environment for the shorter OH groups. However, it was shown in the discussion of the crystal structure of $ZnF_2 \cdot 4H_2O$ that the four long O-H bond lengths represent water molecules in different environments. Three of these are bonded to fluorine atoms and one to an oxygen atom. The four long O-H groups therefore

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	H ₂ O		HI	00	D	0 ₂ O	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	296 K	~100 K	296 K	~100 K	296 K	~100 K	Assignment
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		3625sh,w					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3440s,sh	3419s	3427s	3415s	• • • • •		$\nu_{3}(2,3)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					3428s	3410s	$\nu_{OH}(O(2) - H(6))$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						3325ch w	$\nu_{OH}(O(3) - H(4))$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					3291sh	3298s	$v_{out}(O(3) - H(3))$
$\begin{array}{cccccc} 2257 h, w & 2278 h, s & $r_{u_1}(2,0) - H(5)$, $r_{v_1}(2,0) - 2r_{u_1}(5)$, $r_{v_1}(2,0) - 2r_{u_1}(5)$, $r_{v_1}(2,0) - 2r_{u_1}(5)$, $r_{v_1}(2,0) - 2r_{u_1}(5)$, $r_{v_1}(1,4)$, $r_{v_1}(1,$	3340sh	3333sh.w	3301sh.w	3282sh	020100	52700	$\nu_{1}(3) \text{ or } 2\nu_{2}(H_{2}O)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $,	,		3267sh,w	3279sh,s	$\nu_{OH}(O(2) - H(5))$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	3257sh	3256sh,w					$v_1(2)$ or $2v_2(H_2O)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					2104	3246sh,w	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3156e sh	3154s	3169s sh	31528	.3184s,sn	310/8	$\nu_{OH}(O(4) - H(2))$
3026ah* 3052a* 3053a*	51505,511	51545	51073,311	51523		3063s	$v_{0}(1, -1)$ $v_{0}(0(4) - H(7))$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	3026sh*	3052s*		3053s*			$\nu_3(4)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						\sim 3000sh*	$\nu_{OH}(O(1) - H(1))$
2939sh 2915sh 2505 2673sh 2504sh 2515sh 2516s 2517sh $v_{CD}(O(2, -))$ 2525s 2516s 2517sh $v_{CD}(O(2, -))$ 2455sh 2604sh 2500sh, $v_{V(D_2O(3), -)}$ 2457sh, $v_{CD}(O(2, -))$ 2457sh, $v_{CD}(O(2, -))$ 2457sh, $v_{CD}(O(2, -))$ 2409sh, $v_{CD}(O(2, -))$ 2409sh, $v_{CD}(O(2, -))$ 2409sh, $v_{CD}(O(2, -))$ 2409sh, $v_{CD}(O(2, -))$ 2319s 2337s 2302sh 2567s $v_{CD}(O(1, -))$ 2302sh, $v_{CD}(O(1, -))$ 2302sh, $v_{CD}(O(1, -))$ 2302sh, $v_{CD}(O(1, -))$ 2202sh $v_{CD}(O(1, -))$ 2202sh $v_{CD}(O(1, -))$ 2202sh, $v_{CD}(O(1, -))$ 2205sh 1666s 1663s 1675ch $v_{CD}(1)$ 2205sh 1664sh 1615s, h^{11} 1609sh 1662s 1665s $v_{CD}(1)$ 2205sh 1609sh 1664sh 1615s, h^{11} 1609sh $v_{CD}(2, -)$ 2215sh, $v_{CD}(O(2, -))$ 2215sh, $v_{CD}(O(2, -))$ 2226sh 2243sh 26027sh, $v_{CD}(O(1, -))$ 2205sh 1609sh 1664sh 1615s, h^{11} 1609sh $v_{CD}(2, -)$ 2207sh $v_{L}(D(-)O(2, -))$ 2208s $v_{L}(D(-)O(2, -))$ 2208s $v_{L}(D(-)O(2, -))$ 2208s $v_{L}(D(-)O(2, -))$ 2209s $v_{L}(D(-)O(2, -))$ 2209s $v_{L}(D(-)O(2, -))$ 2200s $v_{L}(D(-)O(2, $	2961sh*	2993s*					v _3(1)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2930sh	2915sh	1672ah				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			207580		25458	25365	$v_{2}(D_{2}O)(2,3)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2526s	2516s	25 100	2517sh	$v_{OD}(O(2) - H(6))$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			2519sh	2504sh		2500sh,w	$v_{OD}(O(3) - H(4))$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					2455sh	2466sh,w	$v_i(D_2O)(3)$ or $2v_2(D_2O)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		2457sh,w	0.05.1			0.445 1	$v_2(4) + v_{Lp}(1,4)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			2435sh	2444s		2445s,sh 2420s,sh	$\nu_{OD}(O(3) - H(3))$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2409sh w		243180		24308,81	$v_{OD}(O(2) - H(3))$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		2403341,44				2401s	$v_1(D_2O)(2)$ or $2v_2(D_2O)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $				2397sh			$v_{OD}(O(1) - H(8))$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2379sh	2367s			$\nu_{\rm OD}({\rm O}(4)-{\rm H}(2))$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						2359s	$\nu_1(D_2O)(1,4)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2319s	2337s	2202ab	2208-			$v_2(2) + v_{L_p}(2,3)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		2302sh w	250281	23068			$V_{OD}(O(4) \sim H(7))$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2502511,**		2288sh			$\nu_{\rm OD}(O(1) - H(1))$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					2299s	2286s	$v_1(D_2O)(1)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					2256sh	2243s	$\nu_3(D_2O)(1)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		2215sh,w	2022-1	2007-1		2020	$v_2(1) + v_{Lo}(1,4)$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			2023sn	2027sn,w		2028W	$\nu_2(HDO)(2) + (HDO)(2,3))$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2000w						$\nu_{Lp}(\Pi DO)(2,3))$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1778sh	1835sh	1777sh,w	1793sh,w	1733sh,w	1710sh	$\nu_2(3)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1721sh					$2\nu_3(MF_2)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1684sh	1691sh	1682sh,w	1671sh,w		1676sh	$\nu_2(4)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1655s	1658s	1000s	1604s	1603s	1000s	$\nu_2(1)$
$\begin{array}{c cccccccccccc} & & & & & & & & & & & & & $	1302w	1005511	1004511	10158,811	1000511,w	101050	$V_2(2)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1273w						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						1270sh	$v_2(D_2O)(3)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $						1240sh	$\nu_2(D_2O)(4)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			1226w		1218s	1219s	$\nu_2(D_2O)(1)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1168eb	1167eh w				11/2sn,w	$V_2(D_2O)(2)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1153sh	1153sh.w					$v_{10}(2,3) + vM - O(3)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1114w					$v_{L_0}(1,4) + vM - O(4)$
$\begin{array}{c c c c c c c } 1005 {\rm sh}, {\rm w} & & & & & & & & & & & & & & & & & & $		1050sh,w					$v_{L\rho}(1,4) + vM - O(1)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0(5)	1005sh,w					
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	965\$n,w	900sn,w 800ch					(2, 2) + iM = O(2)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	871s	877s	873s	889s	8665	888s	$\nu_{L_{\rho}}(2,3) + \nu_{M} = O(2)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0710	815w	0,00	867sh	850sh	863sh	3(142 2)
$\begin{array}{c c c c c c } & & & & & & & & & & & & & & & & & & &$	753sh	769s	768sh	768sh	768sh,w	767sh	$\nu_{L\rho}(1,4)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	700 1	720sh					$v_{L\rho}(2,3)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	/oosn	/035,5h		672eh w			$v_{Lr}(1,4)$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	626s	636%	6365	641s	643s	654s	$\nu_{Lt}(4, 3)$ $\nu_{1}(MF_{2})$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		615sh,w	-000	- ***	- 100		- 1(**** 2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		592sh		-			
$\begin{array}{ccccccc} & & & & & & & & & & & & & & & &$		566sh	556sh	572w	563sh	572s	$v_{L\rho}(D_2O)(1,4)$
$\begin{array}{ccccccc} & & & & & & & & & & & & & & & &$		537sh				525-h	$\nu_{L\omega}(1,4)$
461s 469s ν _{Ls} (D ₂ O)(2,3) 466s 455s ν _{Ls} (D ₂ O)(2,3)	482s	5040		508sh		5558n,w	$v_{Lp}(D_2 U)(2,3)$ $v_1 (7,3)$
466s 455s $\nu_{Lr}(HDO)(2,3)$		20-13		00000	461s	469s	$v_{Lt}(D_2O)(2,3)$
			466s	455s			$\nu_{\rm Lr}({\rm HDO})(2,3)$

Table 4. IR spectra of $ZnF_2 \cdot 4H_2O$ at different temperatures and deuterium contents

* These data were recorded using hexachlorobutadiene mulls on AgBr.



Wavenumbers in cm⁻¹

Fig. 4. The IR stretching bands of the O-H and O-D groups in the hydrate (bottom left) and deuterate (bottom right) as well as isotopically dilute HOD groups in the O-H and O-D stretching ranges (top spectra) at 100 K.



Fig. 5. Graphs of the (a) correlation between r(O-H) in Å in $ZnF_2 \cdot 4H_2O$ versus the ν_{OD} frequencies in cm⁻¹; (b) O-H---Y lengths [R(O---Y)] in Å in $ZnF_2 \cdot 4H_2O$ [4] versus the ν_{OD} frequencies in cm⁻¹; (c-d) (H---Y) lengths [R(H---Y)] in Å in $ZnF_2 \cdot 4H_2O$ versus the ν_{OD} frequencies in cm⁻¹, using (c) exponential and (d) linear fits.

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Table 5. Best fit parameters calculated for v_{OD} versus R(X--Y) and v_{OH}/v_{OD} versus $v_{OH,OD}$ correlation curves. (A and B values for v_{OD} (cm⁻¹) = 2727 - Aexp(-BR), D and E values for $v_{OH}/v_{OD} = 1,360$ -Dexp(-Ev), and m and c for v_{OD} (cm⁻¹) = mR + c)

R,v	A, D, m	B, E, c	Maximum error
R(OY)	8.000 × 10 ⁴	2.061	50 cm ⁻¹
R(HF)	7.882×10^{4}	3.228	$18 {\rm cm}^{-1}$
R(HO)*	7.13×10^{4}	3.06	$33 \text{ cm}^{-1} \text{ (rms)}$
R(HY)	1667	- 402	10 cm^{-1}
. ,	427	1691	4 cm^{-1}
ν _{0H} *	4.674×10^{4}	4.618×10^{-3}	0.002 (rms)
ν _{OD}	3.010×10^{7}	8.885×10^{-3}	0.004

* Graphs fitted by MIKENDA [10].

participate in hydrogen bonds of varying strengths. The graphs of v_{OD} versus R(O---Y)and R(H---Y) represent curves with positive slopes, as is evident from Fig. 5(b-d). The solid lines in Fig. 5(b) and (c) represent correlation curves which have been calculated by least square fits to the experimental points, using functions of the type $v_{OD} = 2727 - Aexp(-BR)$ [10-12]. Some details of the correlations are given in Table 5. This function was first implemented by BERGLUND *et al.* [12] and for infinite hydrogen bond distances the v_{OD} frequency approaches the value of 2727 cm⁻¹ reported for v_{OD} of free HDO molecules [13]. Using this function MIKENDA [10] shows that hydrogen bonds containing halides seem to be remarkably similar if the contact radii of the halides are taken into account. Using the contact radii reported by PAULING [14] and reasonable hydrogen bonds containing I⁻, Br⁻ and Cl⁻ ions as indicated by MIKENDA [10], R(O--F) and R(H--F) values of ~2.76 and ~1.75 Å respectively can be expected. These values agree fairly well with the R(H--F) and R(O--F) values in the ZnF₂·4H₂O structure and the similarity between hydrogen bonds in the halides can therefore be extended to include the F⁻ ions.

In Fig. 5(b-d) the two points at the highest v_{OD} frequencies correspond to O---O and H---O hydrogen bonds. The contact radii of F^- and O^{2-} ions show a small difference and because the scatter in v_{OD} versus R(O---Y) [Fig. 5(b)] is usually large [10], only one function is fitted. The scatter in v_{OD} versus R(H - -Y) is usually smaller than the corresponding v_{OD} versus R(O - - Y) graphs [10] making differentiation between R(H---F) and R(H---O) possible. Two exponential functions are therefore fitted [Fig. 5(c) and in the function at lower frequencies only H---F bonds are taken into account, while the function fitted by MIKENDA [10] to 46 H---O data points was plotted in the higher frequency region. The statistical significance of the H---F fit is not too good and therefore another graph using two straight lines with different slopes in the two frequency regions has been constructed [Fig. 5(d)]. The two regions that can be discerned in this graph can be reconciled with the two types of water molecules. The strongly hydrogen-bonded water molecules $H_2O(1,4)$ give rise to four broad bands of lower frequencies (Fig. 4), while the four narrower bands at higher frequencies are assigned to the distorted and more weakly hydrogen-bonded $H_2O(2,3)$ molecules. Both the exponential and the linear plots were used to estimate R(H--Y) of the Zn compound and in Table 6 these values are compared with the values obtained from crystallographic data. The predictive value of the linear plots in the same frequency region is better than the exponential plots (Table 5) and is used in a subsequent publication to estimate R(H--Y) values in the compounds $MF_2 \cdot 4H_2O$ (M = Fe, Co and Ni) [8].

From the above discussion it is concluded that the frequency differences in v_{OD} and v_{OH} arise mainly from the differences in hydrogen bonding. The $v_{OH,OD}$ modes are therefore assigned using Fig. 5(b-d) as guides.

It is furthermore evident from the slopes of the lines in Fig. 5(b-d) that the stronger hydrogen-bonded ν_{OD} (2397-2288 cm⁻¹) are less dependent on the hydrogen bond lengths than the weaker hydrogen-bonded ν_{OD} (2516-2431 cm⁻¹). The same tendencies

were observed by NOVAK [15] in his study of 25 crystal hydrates. In this study it was also observed that stronger hydrogen-bonded water molecules were always characterized by broader absorption peaks for $v_{\rm OD}$ and $v_{\rm OH}$ in isolated HDO groups, confirming the observations in the present study.

It is evident from Table 6 that the highest and lowest frequencies (2516 and 2431 cm⁻¹) of the higher frequencies are assigned to vibrations of the H₂O(2) groups. The middle two ν_{DO} vibrations of this group are assigned to vibrations involving the H₂O(3) group. It can also be seen in Table 6 that two identical R(H---Y) distances of 1.62 Å have been observed. Here it was assumed that the group with the shortest (O---Y) distance, namely O(1)-F(2) = 2.56 Å, should also have the shortest R(H---Y) distance.

The IR bands of the O-H groups in isotopically dilute HDO groups in $ZnF_2 \cdot 4H_2O$ are also shown in Fig. 4. The assignment of these peaks is given in Table 6. It is evident from Fig. 4 that the higher frequency modes are narrower and can easily be discerned. However, it is more difficult to assign the broader v_{OH} bonds unambiguousy. The assignments of v_{OH} were further investigated by calculating v_{OH}/v_{OD} (Table 6) and plotting it against v_{OH} and v_{OD} [Fig. 6(A) and (b)]. The solid lines in Fig. 6 represent correlation curves of the type $v_{OH}/v_{OD} = 1.36 - D \cdot \exp(-E \cdot v)$ and the values of D and E are given in Table 5. The value of 1.360 serves as a limiting value and corresponds to the isotopic ratio of the free HDO molecule [13]. The solid line in Fig. 6(a) was first calculated by MIKENDA [10] and also fits the data reported in this study confirming the present assignments. Figure 6(b) may prove useful for estimating v_{OH} frequencies if only v_{OD} frequencies are available.

It can be noted from Table 6 and Fig. 6 that v_{OH}/v_{OD} decreases with a decrease in $v_{OH,OD}$ frequencies. BERGLUND *et al.* [16] and MIKENDA [10] found similar tendencies for large data sets and ascribed it to an increase in the mechanical anharmonicity of the isotopically dilute HDO molecules. BERGLUND *et al.* [16] estimate anharmonicity constants $(2\omega_{e\chi_e})$ in the 2900-3700 cm⁻¹ v_{OH} frequency range and if these values are used, $2\omega_{e\chi_e}$ values of between 450 and 300 cm⁻¹ can be estimated for the lower v_{OH} frequencies. For the higher v_{OH} frequencies $2\omega_{e\chi_e}$ will vary between 260 and 220 cm⁻¹.

The isotopic ratio can also be influenced by the lengthening of O---Y during deuterium substitution. This lengthening can be as much as 0.06 Å for strong hydrogen bonds [15] and can cause v_{OD} to be at higher frequencies and v_{OH}/v_{OD} at lower values as expected. The O---O bond length of 2.625 Å in CH₃COOH [15] shows a lengthening of ~0.01 Å upon deuteration and similar lengthenings can be expected for the shorter O---Y bonds in the ZnF₂·4H₂O structure. Previously in this paper it was shown that the difference in the stretching frequencies of HDO were mainly influenced by a difference in hydrogen-bonding [Fig. 5(b-d)]. Using these data a lengthening of ~0.01 Å in O---Y will increase v_{OD} by ~10 cm⁻¹ and decrease v_{OH}/v_{OD} by ~0.005. It can therefore be concluded that the decrease in isotopic ratio with a decrease in stretching frequency arise mainly from the mechanical anharmonicity with a contribution from the lengthening of O---Y upon deuteration.

ν _{OH}				<i>R</i> (HF		
	ν _{OD}	v _{oh} /v _{od}	[4]	Estimated linear	Exponential	Assignments O-HY
3410	2516	1.355	1.93	1.928	1.903	O(2)-H(6)O(4)
3388	2504	1.353	1.90	1.900	1.886	O(3)-H(4)O(1)
3298	2444	1.349	1.75	1.761	1.774	O(3)-H(3)F(2)
3279	2431	1.349	1.74	1.731	1.730	O(2)-H(5)F(1)
	2397	_	1.68	1.678	1.697	O(1)-H(8)F(1)
3167	2367	1.338	1.66	1.661	1.669	O(4)-H(2)F(2)
3063	2308	1.327	1.62	1.626	1.623	O(4)-H(7)F(1)
3000	2288	1.311	1.62	1.615	1.608	O(1)-H(1)F(2)

Table 6. Experimental ν_{OD} frequencies in cm⁻¹ and the estimated R(H--F,O) values in Å for $ZnF_2 \cdot 4H_2O$



Fig. 6. Graphical representations of the ratio v_{OH}/v_{OD} for isotopically dilute HDO groups in ZnF_2 ·4H₂O against (a) v_{OH} and (b) v_{OD} .

In the estimation of $2\omega_{e\chi_{e}}$ [16], ν_{OH} and ν_{OD} were used without taking into account the lengthening of O---Y upon deuteration. This lengthening only occurs with strong hydrogen bonds and the $2\omega_{e\chi_{e}}$ data reported for such molecules [16] may be too large. The $2\omega_{e\chi_{e}}$ values of the strong hydrogen-bonded water molecules in ZnF_{2} ·4H₂O were estimated using $2\omega_{e\chi_{e}}$ data reported in [16] and may also be too large.

The O-H stretching frequency range in ZnF2.4H2O is characterized by the occurrence of very broad and often ill-defined absorption peaks. It is known that the frequency range in which the fundamental O-H stretching modes occur, is complicated by the occurrence of overtones $(2\nu_2)$ and by Evans holes [17]. It is also evident from Fig. 4 that it is not possible to make an unambiguous assignment of the modes here. The features listed at 3333 and 3256 cm⁻¹ could also be assigned to overtones of the bending mode ν_2 . However, it can be assumed with a fair amount of certainty that the most intense peak at 3419 cm^{-1} in the IR spectrum of $\text{ZnF}_2 \cdot 4\text{H}_20$ represents the asymmetric stretching mode v_3 , possibly for both H₂O(2) and H₂O(3). The O-H bands of the isolated HDO groups have already been assigned in Table 4 on the basis of hydrogen bond strengths. Because of the fact that both $H_2O(3)$ and $H_2O(2)$ are very asymmetrically hydrogen bonded, it can be expected that the ν_3 and ν_1 will be largely separated in their frequencies and that their HDO vibrations will be split into two distinct components. Furthermore, these two water molecules resemble one another to a large extent as is indicated by their R(H---Y)and r(O-H) distances. It is therefore very likely that not only their v_3 frequencies, but also their v_1 frequencies, as well as their v_{OH} peaks of the HDO groups, will overlap. These arguments were also used as criteria in the final assignment of bands shown in Tables 4 and 7. The same arguments apply to the O-D stretching frequency range. With the highly asymmetrical $H_2O(3)$ and $H_2O(2)$ groups in the lattice of $ZnF_2 \cdot 4H_2O$, the correlations proposed by SCHIFFER et al. [18] between the v_{OH} (or v_{OD}) frequencies of isotopically diluted HDO molecules and ν_3 and/or $\nu_3 - \nu_1$ do not apply (Table 7).

Table 7. Frequencies of $\nu_{1,3}$ (H₂O, D₂O) of coupled water molecules in ZnF₂·4H₂O at ~100 K as well as the $\nu_{OH,OD}$ frequencies of uncoupled HDO groups ($\Delta\nu_{3,1} = \nu_3 - \nu_1$; $\Delta\nu_{OH(D)} = \nu_{1,3} - \nu_{OH(D)}$)

							$\Delta \nu_{3,1}$			
$\nu(H_2O)$	ν(OH)	$\nu(D_2O)$	v(OD)	$\nu(H_2O)/\nu(D_2O)$	$\Delta \nu_{ m OH}$	$\Delta u_{ m OD}$	H ₂ O	D ₂ O	Assignment	
3419	3410	2536	2516	1.348	9	20	163	91	$\nu_{3}(H_{2}O(2))$	
3419	3388	2536	2504	1.348	31	32	86	70	$v_3(H_2O(3))$	
3333	3298	2466	2444	1.352	35	22			$v_1(H_2O(3))$	
3256	3279	2445	2431	1.352	- 23	14			$\nu_1(H_2O(2))$	
3154	3167	2359	2367	1.337	- 13	- 8			$v_1(H_2O(1),(4))$	
3052	3063	2286	2308	1.335	- 11	- 22	- 102	- 73	$\nu_3(H_2O(4))$	
2993	3000	2243	2288	1.334	-7	- 45	- 161	- 116	$\nu_3(H_2O(1))$	

However, in the case of the H₂O(1) and H₂O(4) molecules, it is interesting to note that upward frequency shifts occurred from $v_1(H_2O(1),(4))$ to $v_{OH}(HDO)$ and $v_3(H_2O(1))$ and $v_3(H_2O(4))$ to v_{OH} . This is in accordance with the correlation of SCHIFFER *et al.* $v_{3,1}(H_2O) = 0.2075 v_{OH} - 669.2$ so that $v_3 > v_1$ if v_{OH} is $> 3225 \text{ cm}^{-1}$, but that $v_3 < v_1$ when v_{OH} is $< 3225 \text{ cm}^{-1}$. In addition to the stretching vibrations, strong bands which can be assigned to combination bands ($v_2 + v_{Lr}$: ca 2337 cm⁻¹), H₂O and D₂O bending vibrations (v_2 : ca 1658, 1219 cm⁻¹), librations (v_L : below 770 cm⁻¹) and MF₂ vibrations ($v_{3,1}$: 877,636 cm⁻¹) can be distinguished (Fig. 2 and Table 4).

The assignment of the librations and MF_2 vibrations are reported in other papers [19, 20]. The results are however summarized for the sake of completeness in Table 4.

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