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Lattice Vibrations of the Water Molecules in $Ba(ClO_3)_2.H_2O$ and $K_2C_2O_4.H_2O$

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Infrared spectra of $Ba(ClO_3)_2.H_2O$ and $K_2C_2O_4.H_2O$ between 40 and 4000 cm^{-1} have been studied at 100 K. The isotopic species H_2O, D_2O, HDO and $H_2{}^{18}O$ have been used to identify the lattice vibrations of the water molecules. Infrared bands at 467, 457 and 396 cm^{-1} for $Ba(ClO_3)_2.H_2O$ have been assigned to rocking, twisting and wagging; bands at 743 and 651 cm^{-1} for $K_2C_2O_4.H_2O$ to wagging and rocking. The twisting mode for $K_2C_2O_4.H_2O$ has not been observed but is predicted to have almost the same wavenumber as the wagging mode (743 cm^{-1}). A translational mode for the water molecule out of the molecular plane has been established at 78 cm^{-1} for $Ba(ClO_3)_2.H_2O$ and at 98 cm^{-1} for $K_2C_2O_4.H_2O$.

Lattice vibrations of water molecules in crystal hydrates are found in the region 300 – 900 cm^{-1} (rotational vibrations) and 50 – 500 cm^{-1} (translational vibrations). This has been verified, for example, in studies of infrared wavenumber shifts on deuterium substitution. Rotational vibrations have been assigned to bands having a wavenumber ratio $\nu_{H_2O}/\nu_{D_2O} \sim 1.36$ and translational vibrations to bands with a ratio ~ 1.04.

A subdivision of the rotational modes can be made assuming rotations about the principal inertial axes of the water molecule, to give the familiar twisting, wagging and rocking vibrations. The translational vibrations can be assumed, to a first approximation, to occur along the principal inertial axes.

It is quite difficult to make unambiguous assignments in these terms using experimental data from infrared and Raman spectra or neutron inelastic scattering, however. Several complications arise, such as the occurrence of bands from several water molecules in the crystal unit cell or low band intensities. The use of single crystals, studied with polarized radiation, should permit correct assignments when the water molecules are found at sites with symmetries C_{2v}, C_s or C_2. Such investigations are rare, however.

The water molecules in $Ba(ClO_3)_2.H_2O$ and $K_2C_2O_4.H_2O$ are found at sites with the symmetry C_2. The space group is $C2/c$ (C_{2h}^6) in both cases.[1,2] The corresponding unit cell groups are thus isomorphous with the point group C_{2h}. In the case of $Ba(ClO_3)_2.H_2O$, single crystal infrared and Raman data exist,[3] whereas only a Raman study has been performed on single crystals of $K_2C_2O_4.H_2O$.[4] Both hydrates have been studied as single crystals using neutron inelastic scattering.[5] In the latter study it was possible to assign the rocking modes definitely. The two remaining rotational modes in each case could not be distinguished. Even with the combined use of Refs. 3 and 5 some ambiguities remain for $Ba(ClO_3)_2.H_2O$ mainly as regards the twisting mode.

In the present investigation we have studied infrared spectra of powders of the two hydrates using the isotopic species H_2O, D_2O, HDO and $H_2{}^{18}O$. From these data and the results of Refs. 3 and 5, we will show that the three rotational vibrations and the translational vibration perpendicular to the water molecular plane can be assigned.

EXPERIMENTAL

Commercial analytical grade $Ba(ClO_3)_2.H_2O$ and $K_2C_2O_4.H_2O$ were used as starting materials for the preparation of the various isotope substituted hydrates. The salts were dried for about 30 h at 140 and 90 °C, respectively, in order to obtain the anhydrous salts. The results were checked by weighing. An appropriate amount of liquid water with the required isotopic composition was then added with a micro syringe. The system of anhydrous salt and water was allowed to reach its equilibrium state in a closed vessel at room temperature. It was found that about two days were enough if the exposed area of the salt was not too small.

The degrees of isotopic enrichment of original D_2O and $H_2{}^{18}O$ liquids were 99.9 and 97 %, respectively.

For the infrared measurements a Beckman IR-9 grating spectrometer was used in the region 400–4000 cm^{-1}. For sample preparation the mull technique was applied with nujol and fluorolube as complementary suspension agents. The hydrates of potassium oxalate were also studied with hexachlorobutadiene mulls in the 600–800 cm^{-1} region. The samples were carried as thin films between plates of KBr or KRS-5.

The far infrared region was scanned using a computer-controlled RIIC FS-720 Fourier spectrometer. An average of several scans (~10) was computed for sample and background (nujol plus polyethene plates) before the ratio was calculated. This reduced the noise to a low level and spectra of good quality were obtained in the region 30–300 cm^{-1}. Between 300 cm^{-1} and 430 cm^{-1} the noise level was somewhat high especially near 400 cm^{-1}. Therefore KRS-5 plates were used to improve the quality of the spectra in this region. The low temperature studies (100 K) were carried out with a Beckman-RIIC VLT2 variable temperature unit.

The spectrometers were calibrated using standard gas bands.[6] The resolution was about 3 cm^{-1} in the region 30–400 cm^{-1} (FS-720 spectrometer) and 2 to 3 cm^{-1} in the region 400–3600 cm^{-1}. For narrow bands the given wavenumbers should be accurate to ± 2 cm^{-1} if registered with the IR-9 spectrometer and ± 1 cm^{-1} with the FS-720 spectrometer. In order to obtain reliable values for isotopic ratios in the low wavenumber region the relevant spectra were plotted together using a Calcomp plotter. It was then found that positions of narrow bands relative to each other could be measured with an accuracy of about ± 0.3 cm^{-1}. At 100 cm^{-1} this corresponds to a maximum error in the isotopic ratios of ± 0.006.

Table 1. Infrared absorption wavenumbers of $Ba(ClO_3)_2.H_2O$, $Ba(ClO_3)_2.D_2O$ and $Ba(ClO_3)_2.H_2{}^{18}O$ in the region 470–40 cm^{-1}.

$Ba(ClO_3)_2.H_2O$		$Ba(ClO_3)_2.D_2O$		$Ba(ClO_3)_2.H_2{}^{18}O$		Assignments
100 K	298 K	100 K	298 K	100 K	298 K	
467 m	451			468 m	451	rocking H_2O
457 w				455 w		twisting H_2O
		437 [a]				out of plane H, HDO
		406 [a]				rocking HDO
396 s	390			395 s	390	wagging H_2O
		362 m	351			rocking D_2O
		340 w				twisting D_2O
		317 [b]				out of plane D, HDO
		292 s	290			wagging D_2O
246 m	235	237 m	225	236 m	224	in plane transl.H_2O,D_2O
		241 [c]				in plane transl. HDO
217 m	208	209 m	200	211 m	203	in plane transl.H_2O,D_2O
184 m	176	183 m	174	183 m	173	External vibrations
172 m	165	172 m	165	172 m	165	
153 m	149	152 m	148	152 m	146	
143 m	139	142 m	139	143 m	140	
136 m	134	136 m	134	137 m	134	
130 s	126	130 s	126	130 s	125	
109 s	107	109 s	106	109 s	106	
97.1 m	95	96.1 m	95	96.1 m	94	
77.6 m	75	76.0 m	74	75.0 m	72	out of plane transl., H_2O,D_2O

s = strong, m = medium, w = weak. [a] Measured using a ratio H/D = 5/95. [b] Measured using a ratio H/D = 95/5. [c] Measured using a ratio H/D = 50/50.

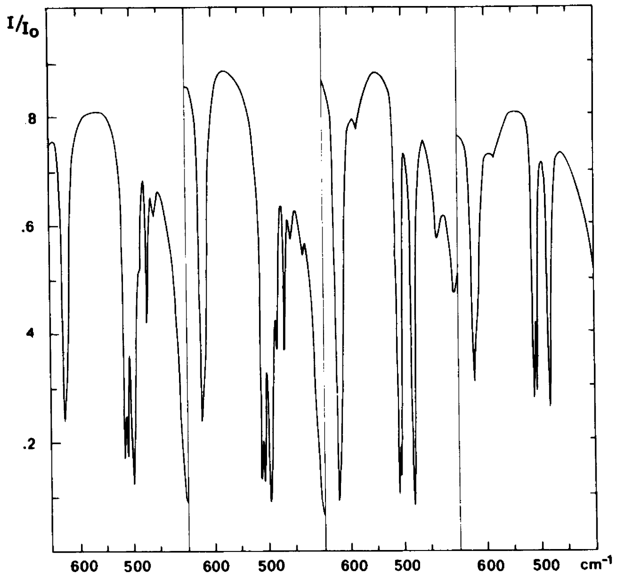

Fig. 1. Infrared spectra (nujol mulls) of $Ba(ClO_3)_2.H_2O$ containing different amounts of deuterium at 100 K in the region of rotational vibrations of the H_2O molecules. From left to right 100, 95, 5 and 1 % H.

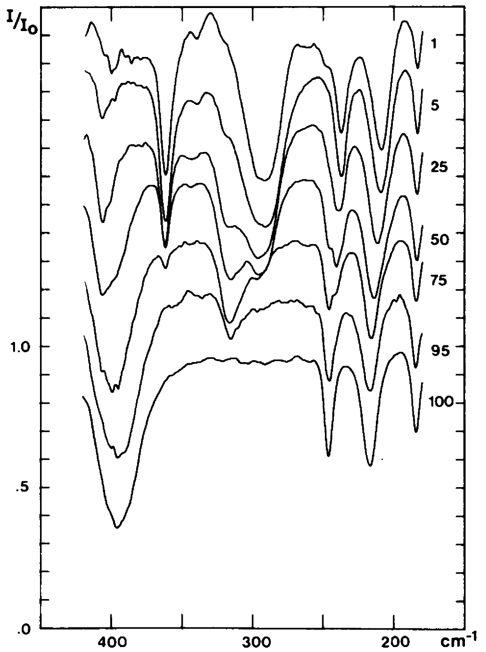

Fig. 2. Far infrared spectra (nujol mulls) of $Ba(ClO_3)_2.H_2O$ containing different amounts of deuterium at 100 K in the region of rotational vibrations of the D_2O molecules. The percentages of H are given in the figure.

RESULTS AND DISCUSSION

Our results for $Ba(ClO_3)_2.H_2O$ in the region above 470 cm^{-1} are in agreement with those of Ref. 3 where survey spectra can be found. The discussion is therefore limited to the low wavenumber region where the rotational and translational vibrations of the water molecule are found. The spectra considered are shown in Figs. 1–3. Wavenumbers and assignments are given in Table 1.

Survey spectra of $K_2C_2O_4.H_2O$ and $K_2C_2O_4.D_2O$ at 100 K between 400 and 3600 cm^{-1} are shown in Fig. 4 and those between 40 and 400 cm^{-1} including that of $K_2C_2O_4.H_2{}^{18}O$ in Fig. 5. Spectra showing the bands from rotational vibrations of the water molecule with different H/D ratios are shown in Fig. 6. Wavenumbers and assignments of the observed bands are found in Table 2. A vibrational analysis in terms of internal and external vibrations together with symmetry correlation diagrams for $K_2C_2O_4.H_2O$ is given in Ref. 4.

In the following the rotational and translational vibrations of the water molecules are discussed separately. Finally, some further aspects of the spectrum of $K_2C_2O_4.H_2O$ are given.

Table 2. Infrared absorption wavenumbers for $K_2C_2O_4.H_2O$, $K_2C_2O_4.D_2O$ and $K_2C_2O_4.H_2{}^{18}O$.

$K_2C_2O_4.H_2O$		$K_2C_2O_4.D_2O$		$K_2C_2O_4.H_2{}^{18}O$		Assignment of fundamental vibrations
100 K	298 K	100 K	298 K	100 K	298 K	
(3436)sh[d]				(3414)sh		
(3351)sh	(3350)sh,b			(3341)sh	(3350)sh,b	
		3249 w,b				OH-stretching HDO
3244 vs,vb	3270 s,vb			3233 vs,vb	3260 s,vb	ν_3 and ν_1,H_2O
(3156)sh				(3130)sh		
		(3092)vw	(3084)vw			
		(3045)vw	(3042)vw			
(2920)w	(2917)w	(2917)w	(2911)w		(2914)vw	
(2751)vw	(2747)vw	(2753)vw	(2745)vw	(2749)vw	(2743)vw	
(2723)vw		(2724)vw		(2725)vw	(2728)vw	
		(2590)sh	(2590)sh			
		2433 s,b	2475 s,vb			ν_3 D_2O
		2387 m,sh				ν_1 D_2O
(1878)w,b	(1868)vw	(1875)vw,b		(1879)w,b	(1868)vw	
1709 w	1690 sh			1705 w	1688 sh	ν_2 H_2O
		(1670)w				
1612 sh	1608 sh	1612 sh		1616 sh	1612 sh	oxalate antisymm. stretching
1598 vs,b	1596 vs,b	1597 vs,b	1595 vs,b	1596 vs,b	1595 vs,b	
(1569)sh	(1568)sh	(1567)sh	(1564)sh	(1568)sh	(1567)sh	
		1489 m[a]	1476 m[a]			bending HDO
(1446)w,b						
(1409)m	(1408)m	(1407)m	(1405)m	(1408)m	(1406)m	
1322 s	1318 s	1322 s	1318 s	1322 s	1318 s	oxalate symm. stretching
1315 s	1310 s,b	1313 s	1310 s,b	1313 s	1309 s,b	
(1299)sh		(1299)sh		(1299)sh		
		1236 m	1225 m			ν_2 D_2O
		(1070)w,vb	(1060)w,vb			
785 s	775 s	775 s	775 s	785 s	775 s	oxalate angle deformation
		771 s	769 s			
		746[b]				out of plane H, HDO
743 s	723 m,b			740 s	723 m,b	wagging H_2O
651 s	620 m,b			648 s	617 m,b	rocking H_2O
		553 s	551 sh			wagging D_2O
		553[c]				out of plane D, HDO
		540[c]				rocking HDO
529 s	526 s	538 w	530 s	529 s	527 s	oxalate angle deformation
525 s		526 s		524 s		
		475 s	454 m,b			rocking D_2O
357 m	353 w	357 sh	349 w	356 m	353 w	oxalate angle deformation
		353 m				
223 s,b	214 s,b	217 s,b	208 s,b	217 s,b	207 s,b	in plane transl., H_2O, D_2O
191 sh		184 sh		184 sh		in plane transl., H_2O, D_2O
174 vs,b	166 vs,b	173 vs,b	165 vs,b	174 vs,b	166 vs,b	external vibrations
138 sh		137 sh		137 sh		
136 m	130 m	135 m	129 m	135 m	129 m	
124 m	117 sh	124 m	116 sh	124 m	117 sh	
97.9 m	95 m	96.7 m	94 m	93.9 m	92 m	out of plane transl., H_2O, D_2O
60 w	56 w	60 w	56 w	60 w	56 w	external vibration

s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder. [a] Measured using a ratio H/D = 50/50. [b] Measured using a ratio H/D = 5/95. [c] Measured using a ratio H/D = 95/5. [d] Wavenumbers within parantheses are used for combination bands.

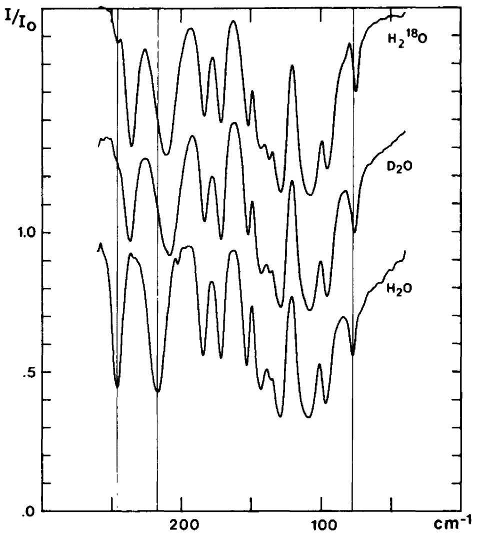

Fig. 3. Far infrared spectra (nujol mulls) of $Ba(ClO_3)_2.H_2O$, $Ba(ClO_3)_2.D_2O$ and $Ba(ClO_3)_2.H_2{}^{18}O$ at 100 K in the region of translational vibrations of the water molecules. Vertical lines are drawn to facilitate the observation of bandshifts.

Rotational vibrations of the water molecules

Inelastic neutron scattering spectra of the hydrates using single crystals have been obtained at 120 K.[5] The spectra were restricted to the region where the rotational vibrations of the water molecules are expected. Using different orientations of the wave vector transfer the authors were able to distinguish the rocking mode (where the hydrogens move in the plane of the molecule) from the twisting and wagging modes (where the hydrogens move perpendicular to the plane).

For $Ba(ClO_3)_2.H_2O$ the rocking mode was found at 477 cm^{-1}. Two additional bands were found at 457 and 398 cm^{-1}. These should correspond to the remaining two rotational modes, but they could not be differentiated in this experiment. In an infrared spectrum the twisting band is expected to have a low intensity[7] since the direction of the dipole moment of the water molecule is unchanged and only changes in the magnitude of the induced dipole moment will give rise to absorption. In the infrared spectrum of $Ba(ClO_3)_2.H_2O$ a band at 395 cm^{-1} (Ref. 3) was assigned as wagging. Due to

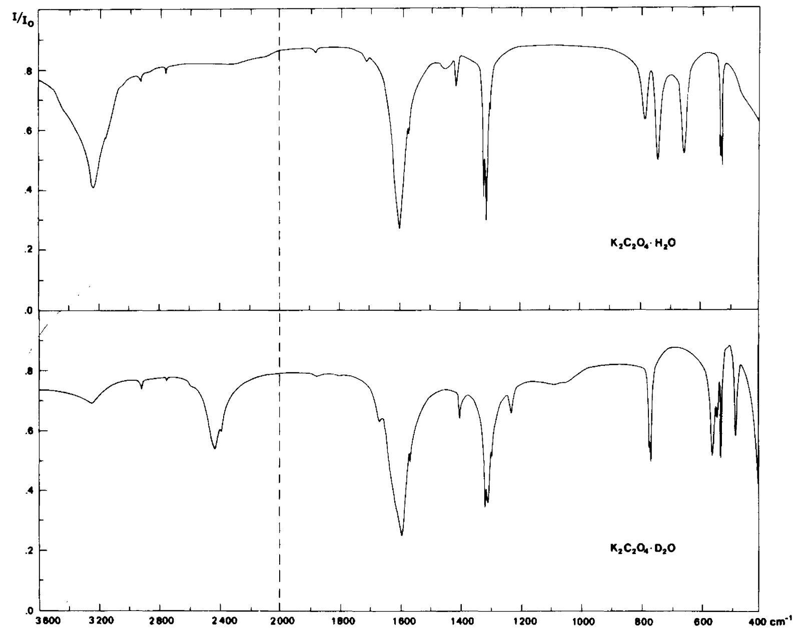

Fig. 4. Infrared spectra of $K_2C_2O_4.H_2O$ and $K_2C_2O_4.D_2O$ at 100 K. Combined spectra from mulls in nujol, fluorolube and hexachlorobutadiene.

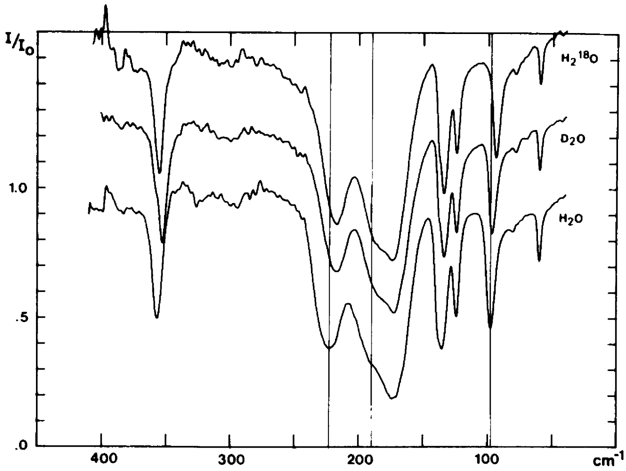

Fig. 5. Far infrared spectra (nujol mulls) of $K_2C_2O_4.H_2O$, $K_2C_2O_4.D_2O$ and $K_2C_2O_4.H_2{}^{18}O$ at 100 K. Vertical lines are drawn to facilitate the observation of bandshifts.

the polarization behaviour of the bands in the infrared spectra a component at 395 cm^{-1} was assigned as twisting. These assignments are thus partly in contradiction with the results of the neutron scattering study.

For $K_2C_2O_4.H_2O$ the rocking mode was found at 644 cm^{-1} in the neutron spectrum,[5] but only one additional band at 738 cm^{-1} was found where two were expected for wagging and twisting. Since intensities of comparable magnitude are expected for twisting and wagging bands in the neutron spectra (the intensities are proportional to the mean square amplitudes of hydrogen motions) an explanation for the single band observed could be that it actually is an unresolved doublet. In the infrared spectra of $K_2C_2O_4.H_2O$[8] a band at 737

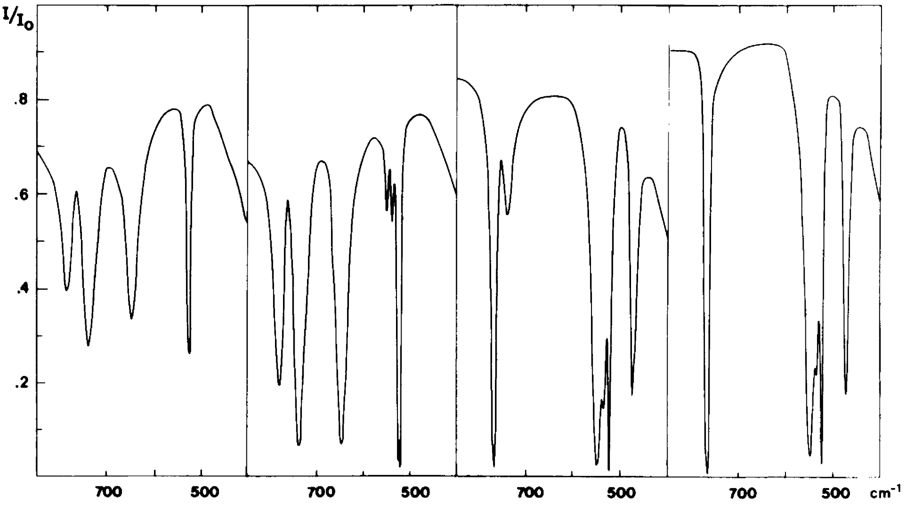

Fig. 6. Infrared spectra (combined from mulls in nujol and hexachlorobutadiene) of $K_2C_2O_4.H_2O$ containing different amounts of deuterium at 100 K in the region of rotational vibrations of the water molecules. From left to right 100, 95, 5 and 1 % H.

cm^{-1} was assigned to wagging but the twisting band was not observed.

In order to resolve the remaining ambiguities we have studied the infrared spectra of $K_2C_2O_4.H_2O$ and $Ba(ClO_3)_2.H_2O$ containing various amounts of HDO. It has been pointed out[9-12] that the use of partially deuterated compounds would be helpful in the assignments of rotational vibrations of water molecules.

We have recently[13] performed a model calculation of the vibrations of a water molecule placed in a simulated crystal environment. The vibrational frequencies and normal modes for H_2O, HDO, D_2O and $H_2{}^{18}O$ were calculated. Some important results found concerning the rotational vibrations will be summarized here. The isotopic ratio ν_{H_2O}/ν_{HDO} was found in the range 1.15–1.22 for the rocking mode. The other two modes of HDO could be described as essentially an out-of-plane H motion (H-mode) and an out-of-plane D motion (D-mode). Furthermore, the wavenumber of the H-mode is close to the average wavenumber of wag (H_2O) and twist (H_2O) and the D-mode close to the average of wag (D_2O) and twist (D_2O).

To obtain a straightforward interpretation of spectra from samples containing HDO, two conditions must be fulfilled. No large correlation field effects may exist and the dispersion of the rotational frequencies as functions of the wavevector must be small. In the present hydrates the correlation field effects are small since the Raman[3,4] and infrared frequencies nearly coincide. The dispersion is small since the bands in the neutron scattering study which represent averages over the wavevectors are relatively narrow.

A schematic representation of the rotational bands discussed in the following is given in Fig. 7.

$Ba(ClO_3)_2.H_2O$. Wag (D_2O) for $Ba(ClO_3)_2.D_2O$ is found at 292 and rock (D_2O) at 362 cm^{-1} in the infrared spectra in agreement with Ref. 3. From Fig. 2 it can be seen that, when the percentage of deuterium is decreased, the intensities of the wag (D_2O) and rock (D_2O) bands are decreased and they finally disappear for 5 % D. At the same time a new band at 317 cm^{-1} appears with increasing intensity relative to wag and rock (D_2O). This band is still visible in the 5 % D spectrum and is hence assigned as the D-mode of HDO. In Fig. 1 two bands are found at 437 and 406 cm^{-1}, in the 5 % H 95 % D spectrum, which are the remaining rotational bands of HDO. The band at 406 cm^{-1} and rock (H_2O) at 467 cm^{-1} give a ratio ν_{H_2O}/ν_{HDO} = 1.15 and the 406 cm^{-1} band is accordingly assigned as rock (HDO). The band at 437 cm^{-1} therefore corresponds to the H-mode of HDO. The H-mode is in fact also visible in Fig. 1 in the 95 % H 5 % D spectrum whereas rock (HDO) is overlapped by wag (H_2O).

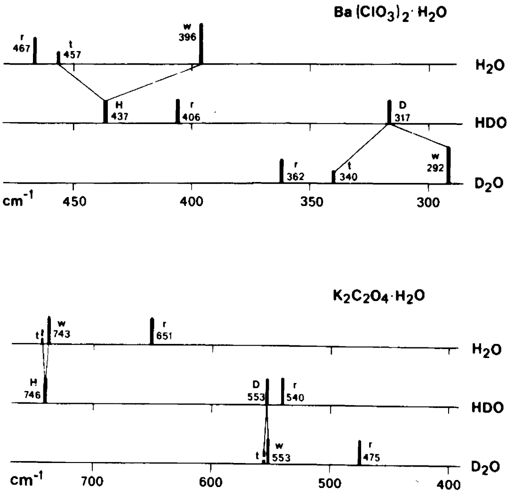

Fig. 7. A summary of the rotational vibration band positions of H_2O, HDO and D_2O for $K_2C_2O_4.H_2O$ and $Ba(ClO_3)_2.H_2O$.

The H- and D-modes of HDO are thus located 41 and 25 cm^{-1} from wag (H_2O) and wag (D_2O), respectively. Since the wavenumber of the H-mode should be close to the average of wag (H_2O) and twist (H_2O) and correspondingly for the D-mode, it is then clear that twist (H_2O) and twist (D_2O) cannot coincide with wag (H_2O) and wag (D_2O) as suggested in Ref. 3. In fact we have observed two new bands in the spectra of $Ba(ClO_3)_2.H_2O$ and $Ba(ClO_3)_2.D_2O$ at 457 and 340 cm^{-1} (see Figs. 1 and 2), which we assign as twist (H_2O) and twist (D_2O). These very weak bands were discovered only because we used thick samples in order to see the bands from the isotopically dilute HDO molecules. The assignment of the band at 457 cm^{-1} to twist (H_2O) is of course strongly corroborated by the peak at 457 cm^{-1} found in the neutron inelastic scattering spectrum.

$K_2C_2O_4.H_2O$. In the infrared spectrum of $K_2C_2O_4.H_2O$ we observed two rotational bands of H_2O at 743 and 651 cm^{-1} (see Fig. 4). The band at 651 cm^{-1} corresponds to the peak at 644±12 cm^{-1} in the neutron inelastic scattering spectrum

and therefore arises from rock (H_2O). The band at 743 cm^{-1} then arises from wag (H_2O) since the band from twist (H_2O) is expected to have a low intensity (see also Ref. 8). In the spectra of samples containing 5 % H and 95 % H in Fig. 6, three bands at 746, 553 and 540 cm^{-1} from isotopically dilute HDO molecules have been observed. The band at 746 cm^{-1} practically coincides with wag (H_2O) and is assigned as the H-mode of HDO. It follows that the D-mode of HDO is expected to have a wavenumber close to that of wag (D_2O) at 553 cm^{-1}. Therefore we assign the HDO band, also at 553 cm^{-1}, to the D-mode. For the reasons discussed above we then assume that the bands from twist (H_2O) and twist (D_2O) are situated very close to the ones of wag (H_2O) and wag (D_2O), respectively. Finally, the HDO band at 540 cm^{-1} should be rock (HDO) giving a ratio $\nu_{H_2O}/\nu_{HDO}=1.21$.

This assignment of the twisting and wagging modes is confirmed by the single peak at 738 ± 12 cm^{-1} found in the neutron inelastic scattering spectrum. The single peak evidently corresponds to an unresolved doublet.

In the neutron scattering experiment[5] two orientations of each hydrate were investigated. This was done to differentiate between in- and out-of-plane motions of the hydrogen atoms. In addition to the main peaks observed and discussed above, some smaller peaks or shoulders were seen. These were explained as arising from two phonon processes involving lower lying modes. Since wagging and rocking each form the representation B_g+B_u under the unit cell group the symmetry permits a coupling between these modes. Such a coupling leads to an out-of-plane component of the motion of the H-atoms for the mainly rocking vibration and an in-plane component for the mainly wagging vibration. We believe that this is the main reason for the additional peaks in the neutron spectra.

Translational vibrations of the water molecules

Below 300 cm^{-1} the IR spectra show essentially three bands that are sensitive to isotopic substitutions in the water molecule. For $K_2C_2O_4.H_2O$ these bands are found at 223, 191 and 97.9 cm^{-1} at 100K (Fig. 5). Corresponding wavenumbers for $Ba(ClO_3)_2.H_2O$ are 246, 217 and 77.6 cm^{-1} (Fig. 3). The latter band was not observed by Bertie *et al.*[3] The intensity of this band increased together with other bands with increasing thickness of the sample. In particular, the band vanished completely if the sample scans were carried out with only nujol between the polyethylene plates. Thus it is ruled out that the band originates from polyethylene.

$K_2C_2O_4.H_2O$. The band at 97.9 cm^{-1} for $K_2C_2O_4.H_2O$ shows a larger shift for substitution with $H_2{}^{18}O$ than with D_2O ($\nu_{H_2O}/\nu_{D_2O}=1.012$ and $\nu_{H_2O}/\nu_{H_2{}^{18}O}=1.043$) (Fig. 5). The increase in the total mass is the same for the two substitutions. Therefore the vibration cannot be a pure translation. To account for the different shifts, a rotational component in the motion must be introduced so that the change of the moment of inertia is larger for the $H_2{}^{18}O$-substitution. The above-mentioned calculation[13] resulted in a low wavenumber vibration in which only the oxygen is vibrating out of the molecular plane. Such a mode has a rotational axis through the hydrogens but can equally well be thought of as translational in character because the centre of mass of the water molecule is not fixed in the vibration. The wavenumber ratio obtained in the calculation was 1.054 for $H_2{}^{18}O$ substitution and 1.000 for D_2O-substitution. If the rotational axis is displaced somewhat towards or away from the oxygen the non-zero shift for D_2O substitution is explained. Actually the model calculations reproduced this situation when the initial restriction implying a stationary environment was relaxed. The existence of a vibration with a low wavenumber and a rotational component as described above is in agreement with the result from the neutron diffraction study of $K_2C_2O_4.H_2O$ at room temperature.[2] Namely, the total out-of-plane amplitude for oxygen was found to exceed that for the hydrogens. Finally, it has been shown[14] that an out-of-plane mode, rotational in character and with a low wavenumber, explains the temperature dependence of the deuteron quadrupole splittings that are measured using a single crystal of $K_2C_2O_4.D_2O$. In view of all this information we assign the vibration at 97.9 cm^{-1} to be an out-of-plane vibration with a rotational component so that the amplitude for oxygen is larger than for the hydrogens.

The band at 223 cm^{-1} is broad and that at 191 cm^{-1} is a shoulder (Fig. 5). The location of these bands is therefore not very precise and accordingly one cannot make definite conclusions from the isotopic ratios.

$Ba(ClO_3)_2.H_2O$. The far IR spectrum of $Ba(ClO_3)_2.H_2O$ has a band at 77.6 cm^{-1} (Fig. 3).

The evidence for an assignment similar to the one for the band at 97.9 cm^{-1} in $K_2C_2O_4.H_2O$ is very much the same for model calculations,[13] neutron diffraction[1] and IR. The isotopic substitutions give the ratios $\nu_{H_2O}/\nu_{D_2O} = 1.021$ and $\nu_{H_2O}/\nu_{H_2{}^{18}O} = 1.035$. Furthermore, the magnitudes of the out-of-plane atomic motions found in the neutron diffraction work are nearly identical for oxygen and hydrogen. This indicates that the rotational component is somewhat smaller as compared to the situation in $K_2C_2O_4.H_2O$. It should also be noted that another band at 97.1 cm^{-1} in $Ba(ClO_3)_2.H_2O$ is shifted to 96.1 cm^{-1} both for D_2O and $H_2{}^{18}O$ substitution. Obviously, some water motion is included in the corresponding vibration.

The remaining bands in $Ba(ClO_3)_2.H_2O$ (246 and 217 cm^{-1}, Fig. 3) have been discussed by Bertie *et al.*[3] One of the bands should be of symmetry type A_u, the other of type B_u. In terms of translational motion of the water molecule the A-type vibration is along the bisector of the OH bonds. According to Ref. 3 Raman data indicated that the band at 246 cm^{-1} is of A-type while the band at 217 cm^{-1} could not be classified from the experiment. Our investigation gives additional wavenumber ratios for $H_2{}^{18}O$ substitution (Table 1), from which one can conclude that the vibration at 217 cm^{-1} has some rotational contribution.

Further aspects of the spectrum of $K_2C_2O_4.H_2O$

For $K_2C_2O_4.H_2O$ Tomar *et al.*[8] observed a broad absorption band with two peaks at 3400 and 3250 cm^{-1} (liquid nitrogen temperature). Those peaks were assigned to the antisymmetric and symmetric stretching vibrations of the water molecule. In our low temperature spectrum (100 K) (Fig. 4) a strong peak appears at 3244 cm^{-1} with shoulders at 3436, 3351 and 3156 cm^{-1}. The spectrum of $K_2C_2O_4.D_2O$ shows a main peak at 2433 cm^{-1} and shoulders at 2590 and 2387 cm^{-1}. Application of the isotopic dilution technique resulted in wavenumbers for the uncoupled OH and OD stretchings at 3249 and 2418 cm^{-1}.[15] These vibrations are expected to be found between respective antisymmetric (ν_3) and symmetric (ν_1) stretching vibrations on the wavenumber scale. Moreover, Schiffer *et al.*[16] have plotted $\nu_3 - \nu_1$ as a function of the uncoupled OH and OD vibrational wavenumbers. Extrapolation of the plots to include the wavenumber regions of $K_2C_2O_4.H_2O$ and $K_2C_2O_4.D_2O$ gives approximate values for $\nu_3 - \nu_1$ of 10 cm^{-1} for H_2O and 60 cm^{-1} for D_2O. In view of this we assign antisymmetric and symmetric stretching motions to the D_2O peaks at 2433 and 2387 cm^{-1}, respectively. Also, we strongly believe that the peak at 3244 cm^{-1} in the $K_2C_2O_4.H_2O$ spectrum is two unresolved bands corresponding to the antisymmetric and symmetric H_2O stretching motions.

A very similar case is found for $LiHC_2O_4.H_2O$.[17] Although the water molecule is on a C_1 site in this compound the OH bonds are nearly equivalent. In the IR spectrum, the D_2O stretching bands are found at 2465 and 2420 cm^{-1}, while in the H_2O stretching region one strong band centred at 3291 cm^{-1} is found. The uncoupled OH (two bands) and OD stretching bands appear at 3297, 3292 and 2451 cm^{-1}.

The water bending vibration in $K_2C_2O_4.H_2O$ has been placed at 1615 cm^{-1} by Tomar *et al.*[8] We observe a band at 1236 cm^{-1} in $K_2C_2O_4.D_2O$ which certainly is due to the D_2O bending vibration. Using intermediate degrees of deuteration a band observed by us at 1489 cm^{-1} must arise from the HDO bending vibration. Moreover, we observe a new weak band at 1709 cm^{-1}. The wavenumber ratio H_2O/D_2O is 1.35 for the free water molecule and for solid hydrates typically around 1.36.[18] The ratio 1709/1236 is 1.38 while the ratio 1615/1236 is 1.31. The band at 1709 cm^{-1} disappears on deuteration while nothing seems to happen around 1600 cm^{-1}. In particular, a weak shoulder at 1612 cm^{-1} in our spectrum is not influenced by deuteration. Instead, a new band appears at 1670 cm^{-1}. We assign the band at 1709 cm^{-1} in $K_2C_2O_4.H_2O$ to the water bending vibration but leave the band at 1670 cm^{-1} in $K_2C_2O_4.D_2O$ unassigned.

We assign bands at 785, 529, 525 and 357 cm^{-1} in $K_2C_2O_4.H_2O$ at 100K to angle deformation vibrations in the oxalate ion. The bands at 529 and 525 cm^{-1} are obviously the A_u and B_u components of the same internal oxalate vibration. On deuteration the band at 785 cm^{-1} splits into two bands at 775 and 771 cm^{-1} while the band at 357 cm^{-1} splits into two bands at 357 (shoulder) and 353 cm^{-1}. The behaviour on deuteration is probably due to a small interference from the water rotational vibrations of which one is of A_u type (twisting) and the others are of B_u type. The small factor group splittings (≤ 4 cm^{-1}) are in agreement with those obtained in the Raman investigation for the A_g

and B_g modes.[4] The band at 357 cm^{-1} in $K_2C_2O_4.D_2O$ has previously been assigned by Fukushima[19] to a rotational vibration of D_2O with the corresponding H_2O band at 524 cm^{-1}. As we have assigned all the rotational and translational vibrations of the water molecule to bands at other wavenumbers, we believe that Fukushima's assignment is not correct.

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