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Hydrogen Bonding. VI. Structural and Infrared Spectral Analysis of Lithium Hydroxide Monohydrate and Cesium and Rubidium Hydroxide Hydrates[1,2]

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Received August 13, 1974 AIC40570M

The infrared spectrum of $LiOH{\cdot}H_2O$ shows, in addition to the stretching and bending modes of OH and H_2O groups, seven bands in the 1000–300-cm^{-1} region. Four of these bands give characteristic shifts upon deuterium substitution and confirm the presence of coordinated water and hydroxide ion in $LiOH{\cdot}H_2O$. On the basis of internal coordinate analysis of the coordinated water and hydroxide subunits of the crystal structure we may assign the various rocking and torsional vibrations of oxygen–hydrogen atoms and the lithium–oxygen lattice vibrations. Unlike other alkali metal hydroxide hydrates the water and hydroxide ions in $LiOH{\cdot}H_2O$ form discrete, planar, hydrogen-bonded $[(OH^-)_2(H_2O)_2]$ anionic units rather than extended chains. RbOH and CsOH also form stable mono- and hemihydrates, the infrared spectra of which contain the rocking and wagging modes of strongly hydrogen-bonded, coordinated water.

Introduction

We have been studying the infrared spectrum of coordinated water in the alkali metal hydroxide hydrates for two reasons. First, these compounds represent intermediate bonding states between the well-characterized clathrate type hydrates[4–6] or intermediate framework hydrates[7] and the tetramethylammonium hydroxide and fluoride monohydrates which we believe[8,9] contain discrete, tightly bound water–anion species as predicted by Jeffrey.[10] Second, by correlation of the infrared spectrum with known crystal structure for lithium hydroxide monohydrate, we hoped to gain insight into methods by which spectral data could be used to derive structural information on hydrates, such as the tetramethylammonium species mentioned above, for which single crystals for diffraction studies are difficult or impossible to prepare.

Although the infrared and Raman spectra of lithium hydroxide monohydrate have been reported in the literature many times,[11–15] no study has included the lower energy region of the spectrum, with the exception of a Raman effect study of lattice motions by Krishnamurti.[15] The region from 1000 to 400 cm^{-1} in the infrared spectrum of a hydrate is of particular interest, as this region asserts the presence of coordinated water and distinguishes it from water of crystallization.[16,17]

The general features of the crystal structure of lithium hydroxide monohydrate have been well established by X-ray diffraction studies;[18–21] these reports, however, did not consider the precise molecular bonding arrangements. We have previously[1] reported—based on our analysis of the data of Alcock—the identification of a discrete, planar, hydrogen-bonded subunit $[(OH^-)_2(H_2O)_2]$ in the crystal. This observation is confirmed by consideration of the recent neutron diffraction studies of Agron, Busing, and Levy[22,23] in which the hydrogen positions are precisely defined and the planar subunits can be clearly seen. The delineation of the spatial arrangements and electronic relationships of the atoms in a unit cell of lithium hydroxide monohydrate allows a clear interpretation of the infrared spectrum.

Experimental Section

Materials. Fisher lithium hydroxide monohydrate and Alfa Inorganics cesium and rubidium hydroxide monohydrates were used without further purification. The cesium and rubidium salts are extremely hygroscopic and were handled in the glove box. $LiOH{\cdot}H_2O$ neutralization equivalent: calcd, 41.95; found, 42.02. $CsOH{\cdot}H_2O$ neutralization equivalent: calcd, 167.92; found, 169.2. $RbOH{\cdot}H_2O$ neutralization equivalent: calcd, 120.49; found, 120.9.

Cesium and rubidium hemihydrates were prepared by heating the appropriate monohydrates at 114° and 0.01 Torr for 3 days over P_2O_5. Additional drying of these salts afforded no further dehydration. Rubidium hydroxide monohydrate melts at the temperature necessary to form the hemihydrate; the hemihydrate which crystallizes out of the sintered mass retains a slight excess of water. $CsOH{\cdot}{}^1/_2H_2O$ neutralization equivalent: calcd, 158.93; found, 158.72. $RbOH{\cdot}{}^1/_2H_2O$ neutralization equivalent: calcd, 111.49; found, 113.1.

Lithium, cesium, and rubidium deuteroxide monohydrates-d_2 were prepared by weighing samples of the appropriate monohydrate in a tared cell, injecting excess 99.7% D_2O through a rubber septum, and evaporating the solvent in vacuo. This process was repeated three times; on the third evaporation D_2O was removed until the weight of the cell indicated the theoretical amount for the deuteroxide monohydrate-d_2. In each case the deuteroxide monohydrate-d_2 was the first completely solid material obtained.

Measurements. Infrared spectra were recorded on a Beckman

Table I. Infrared Spectra of Lithium Hydroxide Monohydrate and Lithium Deuteroxide Monohydrate-d_2[a,b]

$LiOH \cdot H_2O$	$LiOD \cdot D_2O$	ν_H/ν_D	Assignment	Description
3575 s	2635 s	1.36	ν(OH) (b_u)	Hydroxyl O–H str
2965 b, s	2185 b, s	1.36	ν_s(HOH) (a_u), ν_{as}(HOH) (b_u)[c]	Sym and antisym water O–H str
1570 s	1170 s	1.34	δ(HOH) (a_u)	Sym water H–O–H def
1005 s	736 s	1.36	ν_T(HOH) (a_u)	Water torsional vib
860 s	624 s	1.38	ν_{rock}(HOH) (b_u)	Water rocking vib
680, 635 s	490 s[d]	1.34	$\nu_{rock(x,y)}$(OH) (a_u), $\nu_{rock(z)}$(OH) (b_u)[e]	Hydroxyl rocking vib
460 s	450 s	1.02	Lattice mode	
412 s	409 s	1.01	Lattice mode	
336 m	335 m	1.0	Lattice mode	

[a] Values reported in wave numbers (cm^{-1}). [b] Abbreviations used: medium, m; strong, s; broad, b. [c] Both absorptions contained in a broad band. [d] Overlap of the lattice band at 450 cm^{-1} prevents resolution. [e] Not known which peak is associated with which vibration (see discussion).

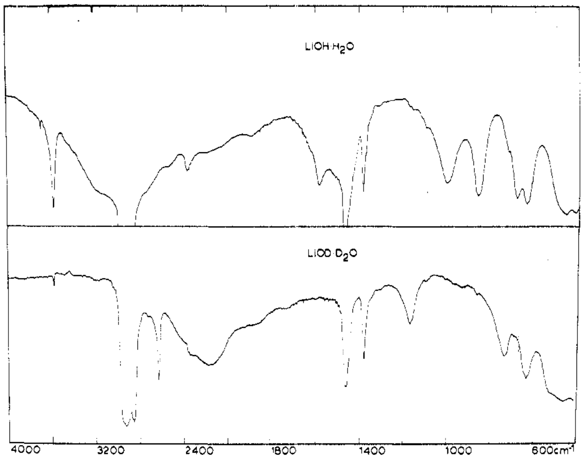

Figure 1. Infrared spectra (Nujol mulls) of lithium hydroxide monohydrate and lithium deuteroxide monohydrate-d_2. Ordinate scale in % *T*.

IR-12 spectrophotometer using CsI plates; mulls were prepared in the glove box using predried Nujol.

Results and Discussion

Infrared Spectrum of Lithium Hydroxide Monohydrate. Table I summarizes the infrared spectral data for lithium hydroxide monohydrate and deuteroxide monohydrate-d_2 and lists the band assignments derived in this work. The infrared spectra of these compounds are reproduced in Figure 1 (4000–400 cm^{-1}) and Figure 2 (750–200 cm^{-1}). Three prominent bands at 3575, 2965, and 1570 cm^{-1} in the spectrum of lithium hydroxide monohydrate correspond to the stretching vibration of the non-hydrogen-bonded[21-23] hydroxide ion (ν(OH)), the symmetric and antisymmetric stretching vibrations of the hydrogen-bonded water molecule (ν_s(HOH) and ν_{as}(HOH)), and the symmetric bending deformation of the water molecule (δ(HOH)), respectively. In addition, the infrared spectrum of lithium hydroxide monohydrate shows seven bands in the 1000–300-cm^{-1} region. Four of these bands at 1005, 860, 680, and 635 cm^{-1} show characteristic shifts upon deuterium substitution and may be attributed to additional vibrational modes of water or hydroxide in this crystal.

The infrared spectra of water molecules or hydroxide ions which are coordinated to metal ions in crystals contain various librational, torsional, rocking, and wagging bands in the 1000–300-cm^{-1} region; these bands correspond to zero-frequency modes in the free molecule;[16,17,24,25] the frequencies, bandwidths, and intensities of these absorptions vary markedly in response to the environment of the water or hydroxyl and can be used, therefore, to differentiate between clathrate or structural water, in which the water molecules are bound in hydrogen-bonded polyhedra, sheets, or ribbons without extensive interaction with the cation, and lattice and coordinated water, in which the water molecules interact through dipole interaction or via dative-bond formation respectively with the cation.[16,26] An analysis of the infrared spectrum of lithium hydroxide monohydrate in this region requires consideration of the atomic and electronic environment of the water and

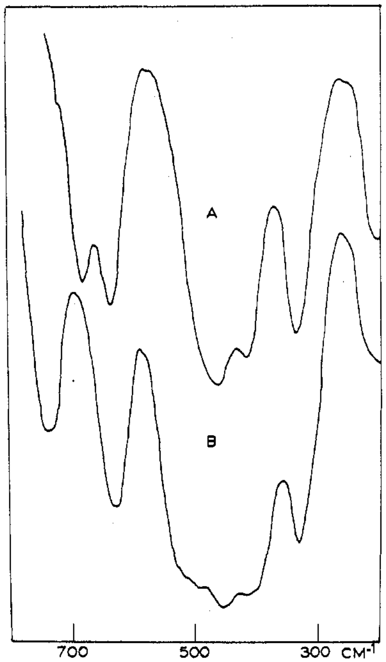

Figure 2. Infrared spectra (750–200 cm^{-1}) of lithium hydroxide monohydrate (A) and lithium deuteroxide monohydrate-d_2 (B). Ordinate scale in % *T*.

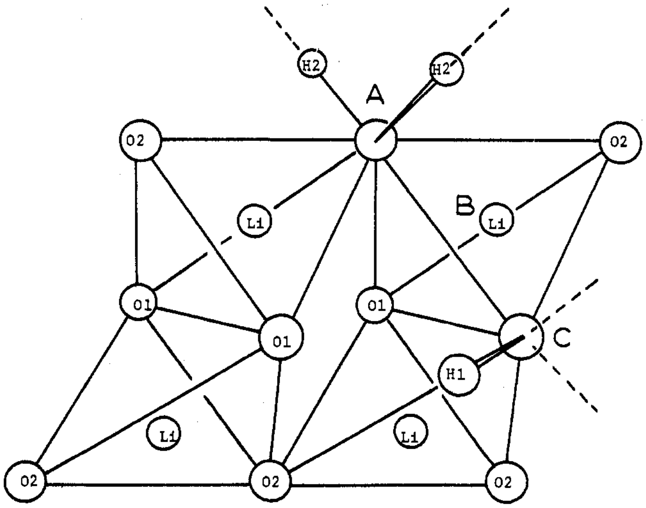

Figure 3. Paired tetrahedral units in lithium hydroxide monohydrate: (A) water oxygens (O2) on C_2 axis; (B) lithium ions; (C) hydroxide oxygens (O1) in mirror plane. Dashed lines represent hydrogen bonds to and from other chains of paired tetrahedra.

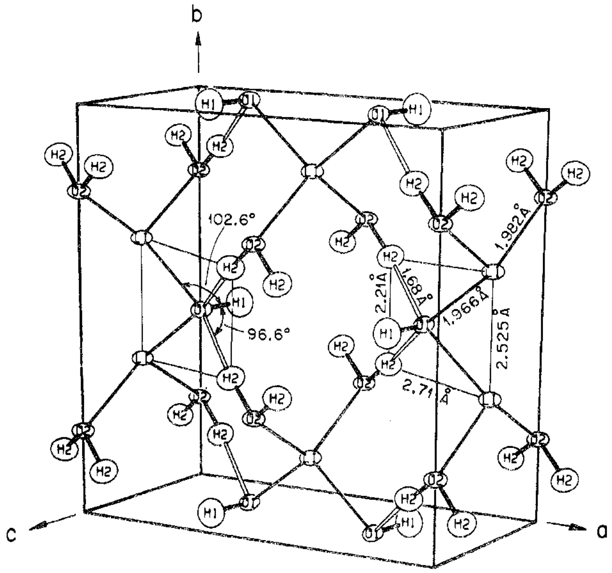

Figure 4. Unit cell of lithium hydroxide monohydrate as determined by neutron diffraction.[24,25] Illustration through courtesy of W. R. Busing of Oak Ridge National Laboratory.

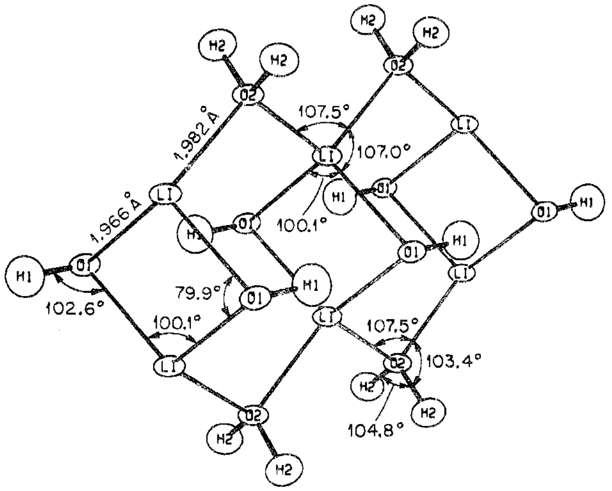

Figure 5. Structural detail in lithium hydroxide monohydrate, from neutron diffraction study.[24,25] Illustration furnished through courtesy of W. R. Busing of Oak Ridge National Laboratory.

hydroxyl groups in the crystal lattice.

Structure of Lithium Hydroxide Monohydrate. Figure 3 depicts the extended structure[18-23] of lithium hydroxide monohydrate, which crystallizes in $C_{2h}{}^3$ (a = 7.4153, b = 8.3054, c = 3.1950 Å; β = 110.107°).[22,23] The structure consists of pairs of tetrahedra of oxygen atoms which share a common edge in a reflection plane; these pairs join corners with adjacent pairs of tetrahedra, thus forming infinite chains of paired tetrahedra along the c axis. Oxygen atoms from hydroxide ions lie in the reflection plane, while oxygen atoms from water lie on C_2 axes and form the shared corners of the tetrahedra. The lithium atoms lie on an alternate set of C_2 axes at the centers of the oxygen tetrahedra. Each water molecule forms two bent hydrogen bonds ($r_{\text{obsd}}(\text{O–O}) = 2.68$ Å) to hydroxide ions lying in the mirror planes of two adjacent chains; each hydroxide ion, in turn, acts as an acceptor in two hydrogen bonds from water. The arrangement of atoms, the bond angles, and the interatomic distances within a single unit cell of the crystal are shown in Figure 4.

A different perspective on the structure is shown in Figure 5, where planar units composed of two lithiums and two hydroxide ions each are seen to be bridged by water molecules.

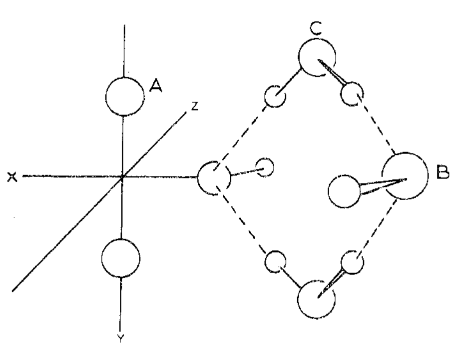

Figure 6. Extended arrangement of water molecules and hydroxide ions in lithium hydroxide monohydrate. The y axis is the twofold axis of the unit cell; the xz plane is the mirror plane of the unit cell: (A) lithium ions; (B) hydroxide ion; (C) water molecule. The lone pair on hydroxide not involved in hydrogen bonding lies on the x axis, directed between the coordinating lithiums.

The water molecules in lithium hydroxide monohydrate are excellently placed for strong coordination to lithium. Each water oxygen has two lithium ions and its own two hydrogens for neighbors in a nearly regular tetrahedral arrangement; the LiOLi angles are 107.5°, and the HOH angles are 104.8°.[24,25] Thus the lone pairs of electrons on the water oxygen are pointed directly toward the electropositive lithium ions. The distance between hydroxide ions in adjacent planar units (Figure 5) is 3.19 Å, too long for effective hydrogen bonding.

The extended relationship of water and hydroxide ions is shown in Figure 6. The top water molecule in one chain of paired tetrahedra and the bottom water molecule in the chain above hydrogen bond to the same hydroxyl groups in two adjacent chains; this creates a hydrogen-bonded planar unit $[(OH^-)_2(H_2O)_2]$.[27] This unit does not lie wholly within the unit cell; however, two incomplete ones can be seen in Figure 4. These planar units are stacked one above the other along the c axis; the plane of the units deviates from orthogonality to the c axis by about 13°.

Examination of Figure 6 shows that the coordination of the hydroxide ion to its two neighbor lithiums is different than the coordination of the water. If we assume tetrahedral orientation of the two hydrogen bonds, the hydroxyl hydrogen, and the lone pair of electrons on the hydroxide ion, then the electron pair occupies an orbital that lies in the mirror plane and is directed between the two lithium atoms. We would expect, therefore, that the hydroxide ion may be bound to the cations either via a three-centered interaction or via a purely electrostatic interaction.

Internal Coordinate Analysis of Lithium Hydroxide Monohydrate. To determine the predicted spectrum of lithium hydroxide monohydrate, we have chosen to treat separately the water and the hydroxide ion, along with their respective coordinating lithium atoms, and thus determine the number and type of vibrations associated with oxygen–hydrogen motions.

The subunit of the crystal chosen for analysis of the water spectrum can be seen in Figure 5. The oxygen atom is bonded to two hydrogens and coordinated to two lithiums in a unit possessing C_2 symmetry; the two planes containing the H–O–H and Li–O–Li angles, respectively, and both containing the C_2 axis deviate from orthogonality by about 10°.[28] This five-atom species of C_2 symmetry will have 15 degrees of freedom which may be described by the reducible representation displayed, based on the cartesian coordinates of the individual atoms.[34]

C_2	E	C_2
Γ_{cart}	15	−1

This representation may be reduced to 7 A + 8 B; in C_2 the rotations and translations belong to 2 A + 4 B, so the vibrational modes will be described by 5 A + 4 B. All of these will be infrared active.

If we choose as five sets of internal coordinates the two O–H bond lengths, the H–O–H angle, the four Li–O–H angles, the two Li–O bond lengths, and the Li–O–Li angle, we may write five reducible representations associated with them. $\Gamma_{\text{O-H}}$ and $\Gamma_{\text{Li-O}}$ each reduce to A + B, $\Gamma_{\text{H-O-H}}$ and $\Gamma_{\text{Li-O-Li}}$ each reduce to A, and $\Gamma_{\text{Li-O-H}}$ reduces to 2 A + 2 B; thus the combination of the five would give 6 A + 4 B. One of these bands, an A mode in $\Gamma_{\text{Li-O-H}}$, is redundant. The vibrations associated with water oxygen–hydrogen vibrations, and thus expected to shift upon deuterium substitution, consist of the previously mentioned symmetric and antisymmetric stretching modes in $\Gamma_{\text{O-H}}$, the deformation mode in $\Gamma_{\text{H-O-H}}$, and two additional bands in $\Gamma_{\text{Li-O-H}}$. These are an in-plane rocking motion of H_2O, ν_{rock}(HOH) (b), and a torsional motion of the subunit around the C_2 axis, ν_{T}(HOH) (a).

The treatment of the hydroxide ion vibrations is similar. The hydroxide ion and its two coordinating lithiums (Figure 6) form a four-atom unit of C_s symmetry; the 12 degrees of freedom on this unit are described by the reducible representation displayed. This may be reduced to 7 A' + 5 A'', which, when

C_s	E	σ_h
Γ_{cart}	12	2

rotations and translations are removed, gives 4 A' + 2 A'' as the vibrational modes of the unit.

Choosing four sets of internal coordinates—the O–H bond length, the two Li–O–H angles, the two Li–O bond lengths, and the Li–O–Li angle—gives four reducible representations associated with these sets of coordinates. Of these, $\Gamma_{\text{O-H}}$ and $\Gamma_{\text{Li-O-Li}}$ each reduce to A', and $\Gamma_{\text{Li-O-H}}$ and $\Gamma_{\text{Li-O}}$ each reduce to A' + A''; there are no redundant modes. The deuterium-sensitive oxygen–hydrogen vibrations of the hydroxyl group are thus a single O–H stretching mode, ν(OH) (a'), and two O–H rocking modes, $\nu_{\text{rock}(x,y)}$(OH) (a'') in which the motion is perpendicular to the mirror plane of the unit cell and $\nu_{\text{rock}(z)}$(OH) (a') in which the motion lies in the mirror plane.

Under the factor group splitting[35] of the C_{2h} unit cell, the number of infrared bands would remain the same; however, each vibration would be split into a Raman-active g band and an infrared-active u band. This has been observed by Krishnamurti[15] for the hydroxyl stretching frequency. When factor group effects are considered, the a and a'' modes described above are designated a_u, and the b and a' modes become b_u under C_{2h}.

Assignments of the Infrared Bands in Lithium Hydroxide Monohydrate. From the preceding discussion, the infrared spectrum of lithium hydroxide monohydrate should show eight deuterium-sensitive bands associated with oxygen–hydrogen motions. Four of these, ν(OH), ν_s(HOH), ν_{as}(HOH), and δ(HOH), are readily located (Table I); ν_s(HOH) and ν_{as}(HOH) are both contained in the broad band at 2965 cm^{-1}. The rocking and torsional modes of the coordinated water molecule in this salt are expected[28–33] to be above 800 cm^{-1} (see following discussion); therefore we assign the bands at 1005 and 860 cm^{-1} to these motions. The remaining pair of deuterium-sensitive bands at 680 and 635 cm^{-1} would then be assigned to the rocking vibrations of the coordinated hydroxide ion.

The C_2 Li_2OH_2 subunit in lithium hydroxide monohydrate can be formally related to a tetrahedral unit of C_{2v} symmetry; a C_{2v} unit at a C_2 lattice site would show the same number and type of infrared-active bands.[35] The infrared spectral assignments of an analogous C_{2v} species, Cl_2CH_2, which lies at a C_2 site in its crystal lattice,[36] have been carefully worked out,[36,37] and we may use comparison to this compound to reach a reasonable assignment of the low-energy bands of water in lithium hydroxide monohydrate. The rocking motion of the CH_2 in solid methylene chloride, ν_7 (b_1),[37] which corresponds[38] to our ν_{rock}(HOH) (b), is found[36] at 891 cm^{-1}, while the torsional vibration about the C_2 axis, ν_5 (a_2),[37] which corresponds to our ν_{T}(HOH) (a), is found[36,39] at higher frequency, 1164 cm^{-1}. We thus assign ν_{rock}(HOH) to the absorption at 860 cm^{-1} in the spectrum of lithium hydroxide monohydrate, and ν_{T}(HOH) to the absorption at 1005 cm^{-1}.

The single, degenerate, deuterium-sensitive rocking band of the hydroxide ion in lithium hydroxide is found[40] at 419 cm^{-1}. The doublet at 680 and 635 cm^{-1} that we have assigned (Table I) to the two hydroxyl rocking motions in lithium hydroxide monohydrate lies at considerably higher energy. This result is expected, since the motion of the ion is constrained by two strong hydrogen bonds; such hydrogen bonding is absent in the anhydrous salt. In the absence of single-crystal studies it is not possible to associate the two vibrations with their specific absorptions.

The internal coordinate analysis carried out herein would formally indicate a number of lithium–oxygen stretching, bending, and deformation vibrations; it is not valid to assign these bands, however, since the lithiums and oxygens are actually part of an extended framework. Through extensive study[40,41] the lithium–oxygen motions of anhydrous lithium hydroxide, in which the lithium also occupies the center of a tetrahedron of oxygen atoms at distances nearly identical with those in the monohydrate, have been identified as coupled lattice type vibrations which are found in a broad region of absorption centered at 450 cm^{-1}. In particular, analysis of the combination bands with the hydroxyl stretching band shows vibrations of lithiums against the oxygen lattice at 495 and 440 cm^{-1} in the anhydrous salt. Lithium hydroxide monohydrate shows three intense bands in the region expected for lithium–oxygen lattice vibrations at 460, 412, and 336 cm^{-1} (Table I and Figure 2); these bands do not shift on deuterium substitution. We assign these bands to lithium–oxygen lattice modes, but do not attempt to associate them with specific motions at this time.[42]

Comparison with Infrared Spectra of Other Hydrate Types. Compounds containing clathrate type water such as ice, gas hydrates, or the higher hydrates of tetraalkylammonium ion salts[4–7] show wide, unstructured librational bands in the infrared spectra; thus in ice,[43] tetramethylammonium hydroxide and fluoride trihydrates,[9] or tetrapropylammonium fluoride dihydrate[44] the librational mode of water is a broad, intense absorption covering the entire region from 1000 to 400 cm^{-1}. We have shown[9] that in structures containing water–anion networks the intensity of the band increases with decreasing hydration number, presumably due to the increased charge density of the framework and concurrent tighter binding of the water.

There is no sharp division between lattice water and coordinated water in crystalline salt hydrates; water molecules can be found in a variety of environments ranging from purely interstitial water to water tightly bound to the cation by covalent bonds. Chidambaram[45] has made an extensive classification based on lone-pair and hydrogen-bond interaction types or the lack thereof. Such salts show water bands in the region 1000–300 cm^{-1} that are distinctly different from the clathrate water spectra.

The mono- and dihydrates of alkali and alkaline earth halides studied by van der Elsken and Robinson[46] contain lattice water;[16] i.e., the water molecules are hydrogen bonded to the anion but do not form dative type bonds with the cation. These salts exhibit two intense bands in the region 600–400 cm^{-1} which arise from rocking and wagging librations of the water molecules.

The transition metal ion hydrates[29–32] contain coordinated

Table II. Infrared Spectra of Cesium and Rubidium Hydroxide Hydrates[a,b]

Hydrate	ν_s(OH)	ν_s(HOH), ν_{as}(HOH)	δ(HOH) region	ν_{rock} region
$CsOH \cdot H_2O$	3500 s	2800 b, s	2000–1550 b, m	975 b, s, 775 sh, 722, 652 s
$CsOD \cdot D_2O$[d]	2600 s	2060 b, s	1310 b, m	725 b, s, 515, 465 s
$RbOH \cdot H_2O$	3539 s	2810 b, s	2400–1500 b, m[c]	1030, 908 b, s, 728 sh, 665, 628 s
$RbOD \cdot D_2O$[e]	2655 s	2200 b, s	1200 s	670, 575 b, s, 430, 392 s
$CsOH \cdot {}^1/_2H_2O$	*f*	3500 sh, 2900 b, s	1700 b, w	970 b, w
$RbOH \cdot {}^1/_2H_2O$	*f*	3450 sh, 2850 b, s	1650 b, w	950 b, w

[a] Values reported in wave numbers (cm^{-1}). [b] Abbreviations used: broad, b; weak, w; medium, m; shoulder, sh; strong, s. [c] It is difficult to estimate the range of this broad, intense band, since it overlaps partly an overtone of water centered at 2400 cm^{-1}. [d] The ratio of ν_H/ν_D for cesium hydroxide monohydrate and its deuterated analog ranges from 1.35 to 1.40. [e] The ratio of ν_H/ν_D for rubidium hydroxide monohydrate and its deuterated analog ranges from 1.28 to 1.60. [f] No free hydroxide stretch in these salts.

water in which the bisector of the two lone pairs on water is directed toward the metal atom.[45] The infrared spectra expected for such hydrates have been calculated[33] using a trigonal-planar MOH_2 model or using normal-coordinate analysis of octahedral $M(OH_2)_6$.[32] Aquo complexes of this type have been shown to exhibit rocking and wagging vibrations along with a metal–oxygen stretch; these bands are observed only when the water molecule acts as both a hydrogen-bond donor and an electron-pair donor in the formation of a coordinate bond with cation. In general, the rocking and wagging bands are found in the region 900–500 cm^{-1} and the metal–oxygen stretch is found in the region 500–300 cm^{-1}. The frequencies of such bands are proportional to the strength of the hydrogen bonds to the anion and the strength of coordination to the metal atom.

Lithium hydroxide monohydrate represents a different class of hydrate, in which the two lone pairs of electrons on water oxygen are each directed toward a different, highly charged univalent ion. The water molecule is thus more rigorously constrained, and the librational bands of water would be expected to lie at higher frequencies than in the previously studied types. This is confirmed by our identification of bands at 1005 and 860 cm^{-1} as water librational modes of lithium hydroxide monohydrate.

Spectra of Rubidium and Cesium Hydroxide Hydrates. The infrared spectra of the cesium and rubidium hydroxide monohydrates, deuteroxide monohydrates-d_2, and hemihydrates are summarized in Table II. The spectra of the monohydrates demonstrate the presence of coordinated water in these compounds; however, the general features of the spectra and their similarity to that of sodium hydroxide monohydrate[47] suggest that the water in these hydrates is not bound as in lithium hydroxide monohydrate. It is likely that the cesium and rubidium hydroxide monohydrates contain extended water–hydroxide ion chains with the water oxygens also coordinated to metal atoms, as in sodium and potassium monohydrates.[48,49]

The cesium and rubidium hydroxide monohydrates show five sets of bands that shift upon deuterium substitution (Table II) and thus are associated with the water and hydroxide ions in the crystals.[50] The O–H stretching band of the hydroxide ion in these salts shows that the ion does not act as a hydrogen-bond donor; however, these absorptions are shifted to lower energy relative to a free hydroxide ion (3700 cm^{-1}) which indicates that the ions act as hydrogen-bond acceptors.[11] The O–H stretching bands of water near 2800 cm^{-1} show strong hydrogen bonding by the water hydrogens, as do the extremely broad bending modes.[51] The water rocking and wagging bands do not show the complex pattern and narrow bandwidth of the lithium hydroxide monohydrate and are typical of those expected for tricoordinate water molecules involved in two hydrogen bonds and a coordinate interaction with a metal atom.[16,17,28-33]

Cesium and rubidium hemihydrates have apparently not been reported before. The water in these compounds is much more tightly held than in the monohydrates and is removed only with difficulty at elevated temperatures. Neither compound shows a band for non-hydrogen-bonded hydroxide ions; the broad absorption in the O–H stretching region shows some structure, which may indicate that several types of hydrogen are represented, but it is clear that all hydrogens in these compounds are involved in strong hydrogen bonds. The rocking regions of the spectra show single broad bands, which suggests that coordinated water species are absent. We predict that the hemihydrates contain either web or ribbon type anion–water frameworks, in which each water acts as a donor to two hydroxide ions and each hydroxide ion acts as a donor to a single water molecule.

Acknowledgment. We wish to thank Susan L. Madeira, Dorothy L. Duffy, and Rodney Halonen for technical assistance.

Registry No. $LiOH \cdot H_2O$, 55622-31-6; $CsOH \cdot H_2O$, 55622-28-1; $RbOH \cdot H_2O$, 55622-29-2; $CsOH \cdot {}^1/_2H_2O$, 55621-93-7; $RbOH \cdot {}^1/_2H_2O$, 55621-94-8.

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Physical Properties of Linear-Chain Systems. II. Optical Spectrum of $CsMnBr_3$[1]

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Received December 17, 1974 AIC40836P

The optical absorption spectrum of the linear-chain, antiferromagnetically ordered compound $CsMnBr_3$ is reported for a range of temperatures from 4.2°K. Magnon side bands, assigned according to a careful set of criteria, are observed in the ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ and ${}^6A_{1g} \rightarrow {}^4E_g(G)$ transitions at temperatures well above the Néel point, $T_N = 85°K$. The anomalously large intensities are explained by considering contributions from both vibronic and exchange-induced electric dipole mechanisms.

Introduction

As is well-known, d–d transitions in octahedral Mn^{2+} compounds give rise to weak absorption band intensities. This condition exists as the transitions are both spin and parity forbidden.[2a] Recently, however, very large intensities have been observed in the absorption spectra of certain manganese salts having the general formula ABX_3 (A = monovalent alkali metal or alkylammonium cation; B = divalent, first-row transition metal ion; $X^- = Cl^-$, Br^-, or I^-).[2b-5] Since these compounds form linear, one-dimensional, magnetically ordered chains,[6] it seems reasonable to assume a cooperative intensity mechanism which can relax spin and parity forbiddenness more effectively than the usual single-ion vibronic and spin–orbit coupling mechanisms.[7]

Tanabe and coworkers[8-13] have proposed a magnon-induced, electric dipole mechanism to account for the anomalous intensities of spin-forbidden transitions in Mn^{2+}. This mechanism has been definitely established for the sharp transition ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$ in $CsMnCl_3 \cdot 2H_2O$.[14] In addition, Day and Dubicki[4] have used the exchange-coupled mechanism and a pairwise-interaction model to explain respectively the intensity and polarization behavior in $(CH_3)_4NMnCl_3$ (TMMC).

While a cooperative mechanism can account for some features observed in the absorption spectra of certain linear-chain manganese salts, it is not a complete explanation. We report the polarized, single-crystal optical absorption spectrum of $CsMnBr_3$ (CMB) in a range of temperatures from 4.2 to 298°K. CMB is antiferromagnetic below 85°K.[15] We show that the observed intensities can be explained by assuming contributions from both vibronic and magnon-induced, electric dipole mechanisms. Below the Néel point the exchange mechanism is more important while above T_N the vibronic mechanism is an important contributor to the intensity.

The spectra are examined for magnon side band transitions, particularly above the Néel point. Only those transitions meeting a careful set of criteria are assigned as magnon side bands.

Experimental Section

Preparation of CMB. Anhydrous $MnBr_2$ was purchased (Rocky Mountain Research, Inc.) and was heated at 200° in a stream of dry HBr gas in order to ensure that the material was truly anhydrous. After cooling, the anhydrous $MnBr_2$ was mixed with an equimolar quantity of CsBr (Research Organic/Research Inorganic Chemical Co.), sealed in a quartz ampoule and zone refined using the Bridgman technique. From the resultant red boule it was possible to cleave single crystals suitable for spectroscopic measurements. It is also possible to grow single crystals of CMB from an equimolar solution of anhydrous $MnBr_2$ and CsBr in freshly distilled concentrated (constant boiling) HBr. The solution was maintained at 50°.

Spectroscopic Measurements. The spectra were measured at 298, 150, 100, 90, 85, 77, 60, 55, 40, 20, and 4.2°K in the spectral range 14,000–40,000 cm^{-1}, using a Cary 14 RI spectrophotometer. Several transitions of special interest were also examined at 10 and 30°K. The single crystals were mounted on aluminum rings which were then inserted into the sample chamber of an Oxford CF 100 cryostat. The temperature was determined and controlled to within ±2°K with an Oxford VC 30 temperature controller calibrated with a digital multimeter. Polarized spectra were obtained by inserting Glan-Thompson prisms in the light paths of the spectrometer's sample and reference chambers. Due to the relatively sharp nature of the transitions, the band positions are accurate to within the resolution of the instrument, ~1 cm^{-1}.