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VERY LOW H-O-H BENDING FREQUENCIES IN THE INFRARED SPECTRA OF SOME CRYSTALLOHYDRATES

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A brief account is given of the work showing that in the spectra of some crystallohydrates (e.g. nickel potassium phosphate monohydrate, copper sulfate monohydrate and related compounds) very low H-O-H bending frequencies are found.

INTRODUCTION

In comparison with the stretching vibrations of H_2O and its deuterium and ^{18}O isotopomers, the region of the bending modes has received relatively little attention. A notable exception is the paper by Falk [1] in which this author has reviewed not only the results obtained by himself and his collaborators but also most of the high-quality work of other investigators (a less thourough survey can be found in Ref. 2). According to this survey, the water bending frequencis in crystallohydrates are found between 1721 and 1582 cm^{-1}, the corresponding value of gaseous water being close to 1595 cm^{-1} [3,4].

Gamo [5] was apparently the first to detect, in the water bending region, the appearence of bands with frequencies which are *much lower* than the gas-phase value. For the infrared spectrum of copper sulfate monohydrate, namely, this author reports two weak bands at 1640 and *1510* cm^{-1}. The existence of bands around 1500 cm^{-1} in the spectra of the monohydrates of various metal(II) sulfates (particularly those of the so-called kieserite* family) was not only confirmed by a number of workers [6,7] but the additional work showed that in many instances the 1500 cm^{-1} band was *the only one* of appreciable intensity. These reports have, however, apparently escaped the attention of Falk [1]. We have also confirmed the existence of low water bending bands in the spectra of copper(II) sulfate monohydrate [8] and in other metal(II) sulfate monohydrates [9].

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* Kieserite is the mineralogical name of $MgSO_4.H_2O$.

Quite some time ago, we came accross other striking examples of very low HOH bending frequencies - those found in the spectra of $NiKPO_4.H_2O$ and some other menbers of the $MKPO_4.H_2O$ family [9,10].

Neither of our reports [9,10] has been widely circulated, however, and thus remained mainly unknown. It is hoped that the present account will help to reverse the present situation as far as these interesting experimental findings are concerned.

EXPERIMENTAL

All investigated compounds were prepared as described in the literature [6,11]. The partially deuterated analogues were obtained using the same general procedure but employing as solvents H_2O-D_2O mixtures of appropriate composition. The infrared spectra were recorded, at room and liquid-nitrogen temperatures (RT and LNT respectively) on a Perkin-Elmer Model 580 infrared spectrophotometer.

RESULTS AND DISCUSSION

INFRARED SPECTRA

$CuSO_4.H_2O$. - As seen in Fig. 1, in the infrared spectrum of this compound only the 1500 cm^{-1} band has an intensity expected for a fundamental, whereas the satelite bands found at higher frequencies are much weaker. It should be noted that the situation is similar in the case of the monohydrates of the kieserite family.

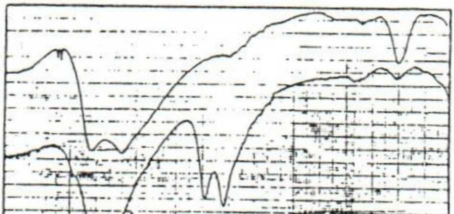

Fig. 1. Infrared spectra of copper sulfate monohydrate and its partly deuterated analogue

$NiKPO_4.H_2O$. - An even clearer picture is observed in the case of $NiKPO_4.H_2O$. As seen in Fig. 2a, namely, here again the only band attributable to a fundamental vibration is the one found below 1500 cm^{-1}, its intensity exceeding by far that of the satelite bands also present in the water bending region.

Other $MKPO_4.H_2O$ compounds. - In the spectra of some of the other members of the $MKPO_4.H_2O$ family, the picture gradually changes on going from the nickel compound to that of manganese in the RT spectrum of which two bands of almost equal intensity

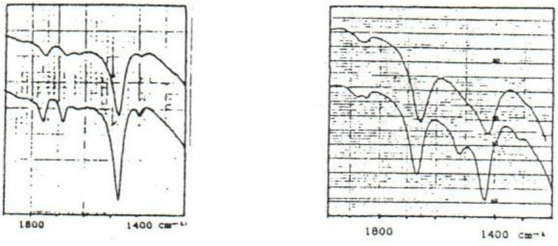

Fig. 2. The H-O-H bending region in the RT and LNT infrared spectra of $NiKPO_4 \cdot H_2O$ (a) and $MnKPO_4 \cdot H_2O$ (b)

appear around 1658 and *1425* cm^{-1}, whereas in the spectrum recorded at LNT at least one further band (around 1520 cm^{-1}) is clearly resolved and additional weak bands appear at lower frequencies (Fig. 2b). The centroid (center of gravity) of the whole feature, however, remains close to 1500 cm^{-1} or somewhat lower.

Deuterates. - Our deuteration studies confirm that the bands found around 1500 cm^{-1} are related to modes involving the water protons both in the case of $CuSO_4.H_2O$ (Fig. 1) and that of $NiKPO_4.H_2O$ (Fig. 3a). The existence, in the spectra of the partly deuterated analogues of $NiKPO_4.H_2O$, of the band around 1300 cm^{-1} is furthermore a proof that the studied compound is a true hydrate. A further confirmation of the identity of this and similar compounds as crystallohydrates can be obtained from the analysis of the spectral picture observed in the OD stretching region (cf. Fig. 3b).

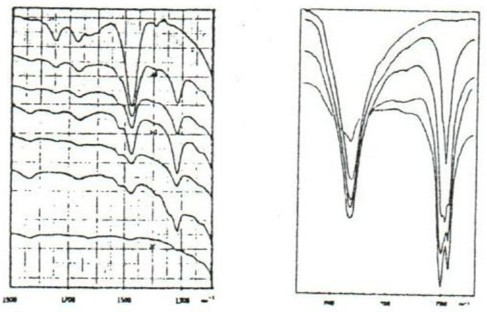

Fig. 3. IR spectra of a series of partially deuterated analogues of $NiKPO_4 \cdot H_2O$: water bending region (a) and stretching region (b)

Other cases of low HOH bending frequencies. - All other known to us cases of systems exhibiting low water bending frequencies are either much less clear or less dramatic than the presented above examples. In fact, it seems that in the rest of the studied cases either a strong band is seen *slightly below* 1600 cm^{-1} or a *complex feature* is present *with a center of gravity* lying lower than the gas-phase value of the HOH bending frequency.

Examples of the first kind have been dealt with by Falk [1] who quotes results both of other workers (for example, the work on the spectra of $CuCl_2.2H_2O$ [12]) and from his laboratory. It was shown that in the case of copper chloride dihydrate the observed infrared band found at 1587 cm^{-1} is only one of the components of a resonance doublet, the uncoupled water bending frequency being higher than 1600 cm^{-1}. Falk, however, shows that even the uncoupled frequency can be lower than that of the water vapour. It should be pointed out, however, that the differences between the observed (or rather - uncoupled) frequencies of the hydrates and the frequency of the bending vibration of water vapour are relatively small (as far as the examples given by Falk [1] are concerned, not more than 15 cm^{-1}).

Among the cases in which the centroid of a complex feature is, beyond doubt, positioned below 1600 cm^{-1}, the compound *trans*-$[CrCl_2(H_2O)_4]Cl.2H_2O$ [14] can be mentioned (Fig. 4). In the spectrum of protiated strontium formate dihydrate the HOH bending region is dominated by the strong band due to the antisymmetric COO stretching vibration. It is obvious, however (Fig. 5), that several new bands, spread out from 1220 to 1000 cm^{-1} or even lower, appear in the spectrum of the deuterate (the bending frequency of gaseous D_2O is 1178 cm^{-1} [5,6]).

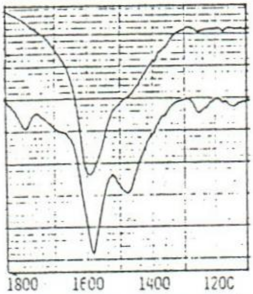

Fig. 4. The water bending region in the RT and LNT IR spectra of trans-$[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$

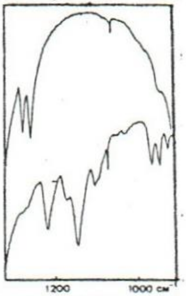

Fig. 5. The D-O-D bending region in the IR spectra of protiated and deuterated strontium formate dihydrate

Summary of the experimental data. - Taken all together, it is obvious that in the infrared spectra of some hydrates low (or even *very low*) H-O-H bending frequencies do indeed exist.

Such a situation is, it must be noted, unusual both from the experimental point of view (in the predominant majority of studied crystallohydrates the water bending bands appear at frequencies which are higher than the gas-phase value) and from that of the available theoretical work. Thus, Falk and his co-workers concluded [3] that the bending force constant should be relatively stable owing to the compromise between its expected increase due to the increased stiffness of the H-O-H angle and decrease due to the elongation of the O-H bonds on bonding of the water molecules in the crystal. Normal-coordinate calculations (for example, those presented by Yukhnevich [16]), on the other hand, suggest that even when the value of the water bending force constant is kept unchanged, the inclusion of new force constants (related to changes of angles around the coordinated and hydrogen-bonded water) is expected to result with an increase of the HOH bending frequency. The more recent model calculations of Eriksson and Lindgren [17] also give higher values for the HOH bending frequency for crystallohydrates than for water vapour.

POSSIBLE REASONS FOR THE LOW WATER BENDING FREQUENCIES

Crystal structure data. - Since the spectral picture must be related to the structural peculiarities (both the spectra and the structure reflect the properties of the potential energy hypersurface), the structures of the compounds exhibiting very low water bending frequencies (which is unusual) must be, in one way or another, also unusual. In trying to find a possible explanation for the origin of very low water bending frequencies one should probably start with an examination of the crystal structure data for the compounds in question.

Unfortunately, the relevant crystallographic data are neither numerous nor of the desired quality. Thus, the crystal structures of the monohydrates of copper sulfate and copper selenate have been determined only by X-ray diffraction [18], whereas the only neutron-diffraction work on the structures of the sulfates of the kieserite family is, to the best of our knowledge, that of Bregeault *et al.* [19] on $MgSO_4.H_2O$. As far as $NiKPO_4.H_2O$ and the isomorphous orthorhombic compounds of the $MKPO_4.H_2O$ type are concerned, the only more or less detailed crystallographic study appears to be the X-ray one by Jovanovski and co-workers [20] (the parameters of the unit cells of the members of the series have been determined by Durif and Averbuch-Puchot [21]). Later attempts to fix the positions of the hydrogen atoms (not determined in the X-ray study) by profile fitting of the powder neutron diffraction data failed.

The data in hands suggest that in $MgSO_4.H_2O$ the water molecules form two equivalent hydrogen bonds with neighbouring sulfate oxygens, the H-Ow-H angle being rather large (approximately 112°) whereas the O...Ow...O angle is much larger (close to 138°). For $CuSO_4.H_2O$ Giester [18] also reports a large value for the O...Ow...O angle (140.53°) but the reported H-Ow-H value is very *small* (83°) rather than large as in kieserite. For a structure determined by X-rays, however, the proton positions are known to be unreliable so that the reported values of the H-Ow-H angle and those of the rest of distances and angles involving protons should be taken with caution.

In $MgKPO_4.H_2O$ [20], on the other hand, the hydrogen bonding scheme is difficult to establish with certainty. Around each water molecule, namely, two pairs of symmetry related phosphate oxygens are found (cf. Fig. 6) at distances 281.1 (Ow...O1) and 291.5 pm (Ow...O3) respectively. The oxygen atoms are positioned around the water molecule in such a way that it is very likely that each water proton forms a bifurcated hydrogen bond. The O1...Ow...O1′ angle is, namely, *very* small (61.6°), whereas the angle O3...Ow...O3′ is not only too large (164.8°) but the O3 oxygens are located in the general direction of the metal ions to which the water molecules are coordinated.

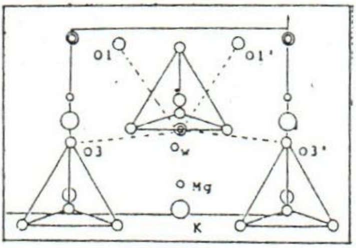

Fig. 6. Crystal structure of $MgKPO_4 \cdot H_2O$

The structural features described above have, at least at first sight, little in common, although admittedly they *are* rather unusual. Furthermore, the nearest neighbours of the water molecules are positioned in such a way as to make it almost certian that the water bending must be appreciably anharmonic. Still, it is not immediately obvious that with structures like these, the investigated compounds should have water bending modes with very low frequencies. Falk has, namely, suggested [1] that the frequency lowering of water bending should be ascribed to water-cation interactions, the latter increasing with increasing cation charge and decreasing cation size. In the studied compounds, on the other hand, the cations are neither small nor highly charged and, besides, the water molecules are not strongly bound to the cations*.

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* It should be noted that in $AlCl_3.6H_2O$ the water bending frequency is normal (higher than 1600 cm^{-1}) although the aluminium ions *are* small and with a high formal charge.

Possible mechanism leading to lowering of the water bending frequencies. - Qualitatively speaking, one of the possible mechanisms leading to low bending frequencies could easily be envisaged. If, namely, the potential well in which the bending takes place is flattened, the energy levels would come closer together and the bending mode would have lower frequency than in the gas phase.

The above mechanism seems to be applicable to the case of $NiKPO_4.H_2O$ if the hydrogen bonds are (as seems highly likely) bifurcated. In this case, namely, it seems that one of the possibilities is to have a potential well of the double-minimum type. Since each of the water protons is likely to be situated between two proton acceptors, bending in either direction (towards the increase *or* the decrease of the HOH angle) will bring the protons closer to the imaginary lines conecting the water oxygen with the oxygens of one of the pairs of proton acceptors. The bending of the water molecules in the crystal would thus seem to be energetically more favorable than the corresponding vibration of the "free" water molecule since in the crystal the bending would be, so to say, "assisted" by the peculiar geometry of the water molecules neighbourhood. If the potential well for the water bending mode *is* of the double-minimum type, then the barrier separating the two minima must be very low since no doubling of the bands is seen (even the correlation-field splitting is not observed). The extreme case of a low-barrier double-minimum potential is, of course, the single-minimum flattened well.

On the other hand, the reported structure of $MgSO_4.H_2O$ is such that the H-O-H bending is likely to be "assisted" in this compound too. If on bending the H-O-H angle is increased beyond its already large value, the energy required to distort the electron density would be partly compensated by the energy gained in the course of the hydrogen bonds becoming more linear. On bending in the oposite direction, the hydrogen bonds become even less linear, but the energy loss is partly compensated by bringing the whole geometry of the water molecules in the crystal closer to that of the free molecules. The situation will be analogous in all cases of coplanar (or nearly coplanar) systems of water having a large H-O-H angle surrounded by proton acceptors located in such a way as to produce an even larger O...Ow...O angle and also in systems characterized by very small H-O-H angles and even smaller O...Ow...O angles (Lutz et al. [22], however have recently stated that small H-O-H angles may be responsible for the unusually *high* water bending frequency which they have found in the spectra of the hydrates of some hydroxides).

A simple model. - In an attempt to have a more quantitative explanation, a simple model of a water molecule with two proton acceptor atoms in its vicinity was treated classically [23]. According to this model, the bending HOH frequencies will be always higher if the hydrogen bonds formed by the water protons are linear, whereas for systems in which non-linear bonds are formed, the water bending frequency could be both higher or *lower*.

MULTIPLE BANDS IN THE H-O-H BENDING REGION

One of the features which has been mentioned several times but was not discussed is the appearence of several deuteration-sensitive bands in the H-O-H bending region.

The weak bands found around 1700 cm^{-1} in the spectrum of $NiKPO_4.H_2O$ are, quite probably, a result of second-order transitions involving the unit-cell modes of librational origin, those to which the observed band around 852 cm^{-1} is due (the origin of the similar bands in the $CuSO_4.H_2O$ spectrum may be analogous). On the other hand, the frequency of the librational fundamental in the spectra of the other members of the $MKPO_4.H_2O$ family is gradually lowered on going from the Ni to the Mn compound and in the spectrum of $MnKPO_4.H_2O$ has a value of about 750 cm^{-1}. In the latter case, the overtones and combinations of the factor-group components of this librational mode should have frequencies close to 1500 cm^{-1}, i.e. to the expected unperturbed value of the fundamental H-O-H frequency. Since there are no symmetry restrictions to the coupling of such second-order transitions with the components of the H-O-H bending mode, the original intensity of the fundamental water bending mode will be distributed between the components of the resulting Fermi-resonance doublet (or, perhaps, multiplet). In such a way the wavenumber of the component at lower frequency can become as low as 1425 cm^{-1}.

It should be noted, however, that in the course of our studies of various crystallohydrates, in the infrared spectra of alums, Tutton's salts and other compounds, more or less regular progressions of bands (all of them sensitive to deuteration) were found extending from 1950 to 1200 cm^{-1} or perhaps even lower [24]. More bands than would have been expected were found in the NH_3 bending region of the spectra of some ammine complexes as well [25]. In all these cases the anharmonic coupling between the corresponding bending fundamental and some low-frequency mode(s) was proposed as a possible reason for the observed spectral picture.

CONCLUSIONS

The experimental observations summarized in the present communication have retained over the years their peculiarity or even uniqueness. The proposed models (both the qualitative and quantitative one) used to explain the appearence of very low H-O-H bending frequencies are, admitedly, very crude and perhaps unsattisfactory in many respects. Obviously, more work (both experimental and, especially, theoretical) should be done in order to have a clearer understanding of the reasons lying behind the appearence of HOH bending bands as low as 1500 cm^{-1}. The present contribution will perhaps initiate such work.

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