

## UNUSUALLY LOW H–O–H BENDING FREQUENCIES. EXPERIMENTAL AND THEORETICAL STUDIES

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**Abstract.** A brief account is given of the experimental and theoretical studies on a group of compounds with the general formula  $M^{II}M^IPO_4 \cdot H_2O$  (where  $M^{II} \in \{Ni, Mg, Co, Mn\}$  and  $M^I \in \{K, NH_4\}$ ). In the Fourier transform infrared (FTIR) spectra of all the these compounds a *very large* red shift of the  $\delta(HOH)$  frequency (compared to that of gaseous water) is observed. Thus, in the spectrum of the protiated cobalt compound, no band of significant intensity is found in the normal  $\delta(HOH)$  region (above  $1600\text{ cm}^{-1}$ ) and, instead, a deuteration-sensitive band of appreciable intensity is seen some  $100\text{ cm}^{-1}$  lower than the gas-phase value. In the case of  $MnKPO_4 \cdot H_2O$  two bands of almost equal intensities appear (above and below  $1600\text{ cm}^{-1}$ ). That unusually low-lying  $\delta(H-O-H)$  band exists in the spectrum of  $MgKPO_4 \cdot H_2O$  as well can be easily deduced on the basis of the over-all similarity of the spectra of the potassium and ammonium compounds. In an attempt to get a deeper quantitative insight into the reasons behind the occurrence of  $\delta(HOH)$  frequencies well below that of "free" water, several quantum chemical models for the  $\delta(HOH)$  potential were proposed, within the finite cluster and finite-field approaches. The vibrational potential energy curves for the uncoupled HOH bending vibrations were obtained from pointwise energy calculations at semiempirical PM3 and *ab initio* Hartree-Fock SCF levels of theory with various basis sets. According to the quantum-chemical results, the overall red shift of the fundamental  $\delta(HOH)$  frequency in the studied systems may be basically attributed to variations in the harmonic force constant ("flattening of the potential well"), while the vibrational anharmonicity is of much lesser importance.

### Introduction

The crystalline hydrates are an interesting class of compounds to the study of which the efforts of a research group at the Institute of Chemistry at the Faculty of Science in Skopje have been devoted for several decades. The main research tool of the group has been infrared spectroscopy supplemented, when possible, with Raman spectroscopy and X-ray diffraction. In recent years, quantum chemical calculations have been carried as well providing a deeper understanding of the observed phenomena. The choice of infrared spectroscopy as the preferred experimental tool was based on the availability of infrared spectrometers, on the one hand, and on the general acceptance of the fact that vibrational spectroscopy has proven to be one of the most useful tools for a study of phenomena related to hydrogen bonding, on the other. Obviously, water in crystalline hydrates is hydrogen bonded although other interactions (e.g. those with the metal cations and the force field in the crystal in general) also play a significant role. It is, thus, only natural that considerable attention has been paid to the vibrational spectra of crystalline water in many parts of the world.

It should be noted that, generally, the water stretching spectral region has been studied in much more detail than the bending one. A particularly important tool has been provided by the introduction (several decades ago) of the study of *isotopically isolated water molecules*. Experimentally, this is usually done by studying the spectra of samples containing a few percent of deuterium so that a small amount of H–O–D molecules surrounded by H–O–H molecules exist in the structure. Pertaining our present discussion, it should be noted that the method of isotopic isolation provides a safe criterion for ascertaining that a given compound does indeed contain water molecules and not oxonium ions. In the former case, namely, for each crystallographically distinct water molecule under normal circumstances a band is found above  $1400\text{ cm}^{-1}$ .

Falk has beautifully summarized the account of the work done on crystalline hydrates up to the early eighties in his much quoted review [1]. An overview of the problems concerning the water bending region (especially the occurrence of very low  $\delta(\text{H–O–H})$  bands in crystalline hydrates) has been given in ref. [2] where a rather extensive list of references appears as well. Thus, only the most pertinent points will be briefly summarized in the present paper.

It has been found that in most of the studied hydrates the bands due to the  $\delta(\text{HOH})$  modes appear at *higher* frequencies than in “free” water but opposite examples exist as well. As found by us, the  $\delta(\text{HOH})$  modes may not only be *red-shifted* in comparison with gaseous water, but this shift can sometimes be *very large*. The most striking examples of the latter kind are provided by the spectra of the  $\text{MKPO}_4\cdot\text{H}_2\text{O}$  type compounds ( $M \in \{\text{Ni}, \text{Co}, \text{Mg}, \text{Mn}\}$ ) and of their ammonium analogues. The first assignments of these unusually low water bending modes date from almost three decades ago [3], but the findings have not been widely circulated until recently [2]. However, only a tentative and intuitive explanation of such large red shifts of the  $\delta(\text{HOH})$  modes in the mentioned compounds has been proposed, based mainly on classical considerations. In order to provide a more thorough theoretical basis for the explanation of the experimentally observed trends, a computational study of the water bending potential has been undertaken. What follows will be a summary of the published and still unpublished work.

It should be mentioned that it is somewhat unfortunate that the X-ray crystal structure of only  $\text{MgKPO}_4\cdot\text{H}_2\text{O}$  has been determined<sup>1</sup> [4] but all of the investigated compounds are thought to be at least isostructural. It was found that  $\text{MgKPO}_4\cdot\text{H}_2\text{O}$  crystallizes in the space group  $Pmn2_1$  ( $C_{2v}^7$ ), with two formula units per unit cell. The water molecules are situated on sites with  $C_s$  symmetry and the inspection of the nearest neighbors clearly shows that the crystallographic symmetry plane coincides with the molecular symmetry plane perpendicular to the H–O–H one. Each water molecule is surrounded by six nearest neighbors – four phosphate oxygen atoms of two crystallographically different types supplemented by one divalent and one monovalent ion located on a plane perpendicular to that of the water molecule. The  $\text{O}_w\cdots\text{O}$  contacts with the closer-lying phosphate oxygens are unfavorable for formation of hydrogen bonds since these atoms are located in the same general direction (of course, not in the same

<sup>1</sup> The positions of the protons were not determined.

plane) as the two potassium cations. On the other hand, the  $O-O_w-O$  angle with the other pair of phosphate oxygens is quite small (only  $64.3^\circ$ ) and, thus, the hydrogen bonds are extremely unlikely to be formed with these two oxygen atoms only. All in all, it is practically certain that the two hydrogen bonds are symmetrically bifurcated. It seems that the arrangement of the potential proton acceptors around the water molecules such as that found in the case of the  $MKPO_4 \cdot H_2O$  compounds is important in explaining the origin of the very low  $H-O-H$  frequencies and may even be one of the prerequisites for the appearance of very low water bending frequencies.

### Experimental

The compounds of the  $MKPO_4 \cdot H_2O$  type were synthesized according to the method described in ref. [3]. Magnesium ammonium phosphate monohydrate (synthetic dittmarite) was synthesized according to the method described by Kiehl and Hardt [5]. The deuterated analogues were obtained by the same route, only using  $H_2O-D_2O$  mixtures of appropriate composition as solvents.

Fourier transform infrared (FTIR) spectra were recorded of KBr pellets at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) on a Perkin-Elmer System 2000 FTIR interferometer. A Graseby-Specac variable temperature cell was used for the low-temperature measurements. The working resolution of the instrument was  $4\text{ cm}^{-1}$ . In order to obtain a good signal-to-noise ratio, 64 scans were collected and averaged at LNT, while often 32 scans appeared to be enough at RT. For acquisition of spectra and manipulations on them the GRAMS ANALYST 2000 [6] and GRAMS 32 [7] packages were used.

The bending potential of "free" water molecule and a water molecule which is a building block of the structure of a crystalline hydrate (this latter type of  $H_2O$  molecules will be denoted as "in-crystal" water molecule) was theoretically studied at semiempirical and *ab initio* HF SCF levels of theory. The semiempirical approach was based on the PM3 Hamiltonian, while various basis sets were used for orbital expansion in the *ab initio* techniques. These included the rather large, triple zeta quality 6-311++G(3df,3pd) basis augmented with diffuse functions, and the LANL2DZ basis (which includes the Los Alamos ECP plus DZ on K, P, Mg and D95 on O and H). Scans of the intercept through the potential energy hypersurface of a water molecule corresponding to the  $\delta(\text{HOH})$  vibrational motion have been performed with pointwise energy calculations. In order to simulate the crystalline surrounding of the water molecule in compounds of the  $MKPO_4 \cdot H_2O$  type, three approaches were adopted. Within the first one, the nearest-neighbor atoms in the  $MgKPO_4 \cdot H_2O$  crystal (as found by X-ray diffraction [4]) were explicitly included in the calculations. In the second approach, the crystalline water molecule was embedded in an array of point charges distributed in the same way as the nearest-neighbor ions in the crystal structure of  $MgKPO_4 \cdot H_2O$ . A study of a water molecule placed in finite electrostatic fields with various strengths oriented both along (parallel and anti-parallel) the  $C_2$  axis and perpendicularly to the water molecule plane was the essence of the third approach.

The obtained potential energy curves were fitted to a fourth order polynomial in  $(\alpha_{\text{HOH}} - \alpha_{\text{HOH},e})$  of the form:

$$V = V_0 + \frac{1}{2} k_{\alpha\alpha} r_{\text{OH},e}^2 (\Delta\alpha)^2 + k_{\alpha\alpha\alpha} r_{\text{OH},e}^3 (\Delta\alpha)^3 + k_{\alpha\alpha\alpha\alpha} r_{\text{OH},e}^4 (\Delta\alpha)^4 \quad (1)$$

( $\alpha_{\text{HOH},e}$  and  $r_{\text{OH},e}$  being the corresponding equilibrium values), and the one-dimensional vibrational Schrödinger equation was solved using the second-order stationary perturbation theory (SOPT). All calculations were carried out with the Gaussian94w series of programs [8].

### Results and Discussion

The LNT spectra of  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{MnKPO}_4 \cdot \text{H}_2\text{O}$  are given in Fig. 1. It is easy to notice that the overall appearance of the spectra is similar, except for the regions where the bands due to internal and external water vibrations occur.

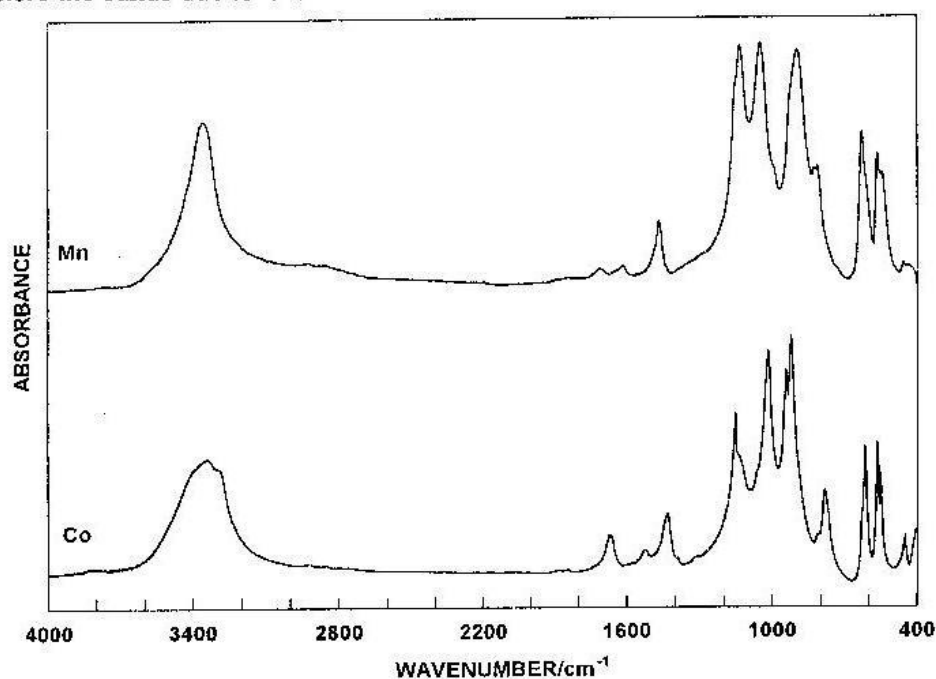


Fig. 1. Infrared spectra of  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{MnKPO}_4 \cdot \text{H}_2\text{O}$

In the  $\nu(\text{OH})$  region, even at LNT, only one band appears in the case of the Co compound (the situation is similar in the spectra of  $\text{NiKPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ ) which implies that the H–O–H angle should not be much different from  $90^\circ$ . Namely, within the classical GF approach, the following approximate solutions of the vibrational secular equation may be straightforwardly obtained when the coupling constant  $k_{\delta\text{H}}$  is negligibly small and the  $\nu_2$  mode frequency is significantly smaller than that of  $\nu_1$ :

$$\lambda_3 = \left( 1 + 2 \frac{m_{\text{O}}}{m_{\text{H}}} \sin^2 \alpha \right) \frac{k_1}{m_{\text{O}}}; \quad \lambda_1 = \left( 1 + 2 \frac{m_{\text{O}}}{m_{\text{H}}} \cos^2 \alpha \right) \frac{k_1}{m_{\text{O}}} \quad (2)$$

( $m_i$  are the corresponding relative atomic masses,  $k$  is the harmonic force constant, and  $\alpha$  is the half the HOH angle). Thus, when  $\alpha = 45^\circ$  (that is, when the H–O–H angle is  $90^\circ$ ) the two roots would be accidentally degenerate.

The corresponding region in the case of  $\text{MnKPO}_4 \cdot \text{H}_2\text{O}$  is significantly broader while in the spectrum of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  the situation is complicated by the appearance of bands due to the stretching vibrations of the ammonium ions. This region will not be discussed any further.

In the region above  $1600 \text{ cm}^{-1}$  where ordinarily bands due to the  $\delta(\text{HOH})$  motions would be expected (Fig. 2), no band of appreciable intensity is present in the case of the Co compound and of its Ni and Mg analogues. On the other hand, a rather intense band appears at  $1464 \text{ cm}^{-1}$  in the LNT FTIR spectrum of  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$ . Two much weaker "satellite" bands also exist (at  $1708$  and  $1614 \text{ cm}^{-1}$ ), the situation in this respect being analogous to that encountered in the case of  $\text{NiKPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ . In the corresponding region in the spectrum of  $\text{MnKPO}_4 \cdot \text{H}_2\text{O}$  two bands with almost equal intensities appear (at  $1661$  and  $1433 \text{ cm}^{-1}$ ), accompanied by a much weaker band at  $1525 \text{ cm}^{-1}$  (Fig. 2). The situation with the Ni compound is almost identical with that found in  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$  and the spectral picture in the case of  $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$  may be considered as intermediate between that found in  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{MnKPO}_4 \cdot \text{H}_2\text{O}$ .

All mentioned bands in the spectrum of  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$  – the intense one and its weaker "satellites" – are deuteration sensitive (Fig. 3). It seems clear that the H–O–H bending must be responsible for the appearance of the strongest band in the region, whereas the most likely explanation for the "satellite" bands is that they are due to second-order transitions of fundamental modes which themselves are deuteration sensitive.

There is one clear candidate for such a fundamental – the band at around  $813 \text{ cm}^{-1}$  originating from one of the water librational modes whose overtone is of the right symmetry (A1) to interact with one of the factor-group components of the  $\delta(\text{HOH})$  fundamental. The frequency of such an overtone ( $2 \times 813 = 1626$ ) would be appreciably higher than that of the strong band attributed to the fundamental H–O–H bending and, thus, the vibrational coupling should be weak<sup>2</sup>.

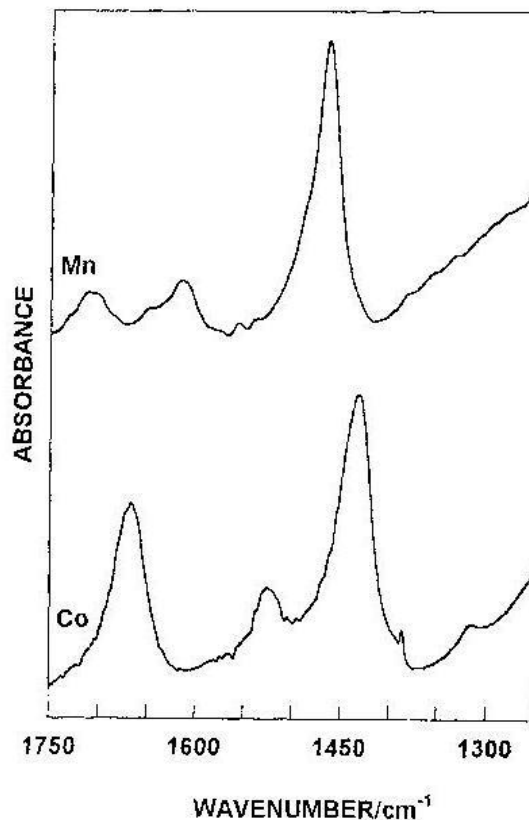
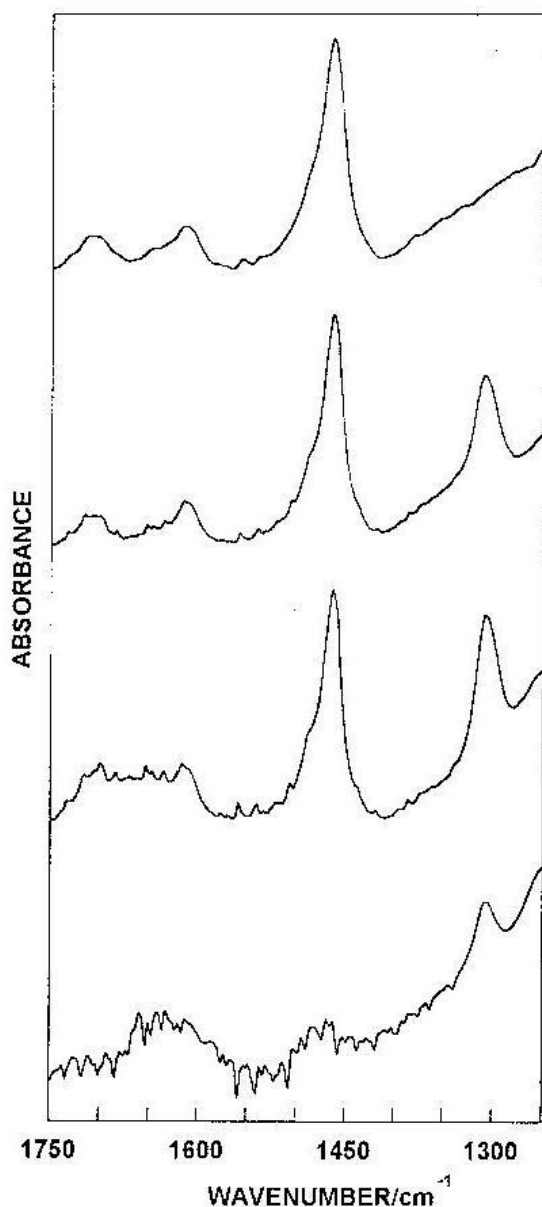


Fig. 2. Infrared spectra of  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{MnKPO}_4 \cdot \text{H}_2\text{O}$  in the HOH bending region

<sup>2</sup> The presence of *two* "satellite" bands can be explained by assuming that the at least one of them is due to a combination of the  $\delta(\text{HOH})$  mode with some low-frequency mode.



**Fig. 3.** The HOH/HOD bending region in the spectrum of partly deuterated  $\text{CoKPO}_4$  (the deuterium content increases from top to bottom)

since it should fall in the region where the strong bands due to the antisymmetric  $\text{PO}_4$  vibrations appear.

Were it not for the fact that  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  is isomorphous with  $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$  and thus the spectral features (other than those arising from ammonium ion vibrations)

Such is not the case with the manganese compound and this is reflected in the observed spectral picture. Namely, in the  $\delta(\text{HOH})$  region of the spectrum of  $\text{MnKPO}_4 \cdot \text{H}_2\text{O}$  two bands with almost equal intensities appear (at  $1661$  and  $1433 \text{ cm}^{-1}$ ), accompanied by a much weaker band at  $1525 \text{ cm}^{-1}$ .

The existence of two, almost equally intense, bands may be rationalized by taking into account the fact that the corresponding librational band has a much lower frequency ( $\approx 783 \text{ cm}^{-1}$ ) than in the spectrum of the cobalt compound and thus the conditions for an effective Fermi resonance are more favorable.

It is important to emphasize that the strongest Fig. 1. Infrared spectra of  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{MnKPO}_4 \cdot \text{H}_2\text{O}$  band in the  $\delta(\text{HOH})$  region of the  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$  spectrum appears at more than  $100 \text{ cm}^{-1}$  below the "low limit" mentioned in the much quoted Falk's review [1]. Thus, it is significantly red-shifted, not only in comparison with the "free" water but also with the majority of crystalline hydrates studied so far.

In the spectrum of the slightly deuterated  $\text{CoKPO}_4 \cdot \text{H}_2\text{O}$  isotopomer (Fig. 3), a band, attributed to the  $\delta(\text{HOD})$  mode, appears at  $1309 \text{ cm}^{-1}$ , which at first gains in intensity upon increase of the deuterium content (up to about 50%), and then gradually disappears. It is not possible to unambiguously determine the exact location of the band due to the  $\delta(\text{DOD})$  mode

should be similar, it would be difficult to locate the  $\delta(\text{HOH})$  band there. In fact at least four bands are found in the infrared spectrum of protiated  $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$  (the LNT frequencies are 1662, 1539, 1482 and  $1432\text{ cm}^{-1}$ ) of which the latter two have frequencies close to that of the strong band in the spectrum of  $\text{CoKPO}_4\cdot\text{H}_2\text{O}$ . In the spectra of the slightly deuterated analogue three prominent bands (at  $\approx 1316, 1300$  and  $1283\text{ cm}^{-1}$ ) appear in the region where the N–D bending vibrations of isotopically isolated  $\text{NH}_3\text{D}^+$  ions are expected but where, by analogy with the compounds of the  $\text{MKPO}_4\cdot\text{H}_2\text{O}$  type the  $\delta(\text{HOD})$  vibration would also appear. In fact, the frequency of the highest of these bands is almost equal to that found in the spectrum of slightly deuterated  $\text{NiKPO}_4\cdot\text{H}_2\text{O}$  [2]. This should be no big surprise since the spectra of protiated  $\text{NiKPO}_4\cdot\text{H}_2\text{O}$  and  $\text{MgKPO}_4\cdot\text{H}_2\text{O}$  are quite similar and this is also true for the spectra of  $\text{MgKPO}_4\cdot\text{H}_2\text{O}$  and  $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$  so that the  $\delta(\text{HOD})$  bands in the spectra of all these compounds should appear at similar frequencies.

Taken all together, it is possible to explain in a rational manner the spectral subtleties of the spectra of the three studied compounds. However, the fundamental problem – the *reasons* behind the appearance of H–O–H bending frequencies lower than the gas-phase value – still remains only partly solved. In ref. 2 it was argued that with a geometry of the water molecules and its neighborhood such as that which exists in the structure of  $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ , the H–O–H bending in each direction (towards increase of the HOH angle or in the opposite direction) would be assisted either by the increased linearity of the hydrogen bonds or by the HOH angle coming closer to its equilibrium value.

Although such an intuitive and qualitative explanation seems to be acceptable for the time being, in order to shed some light on this problem, the quantum chemical calculations described above were undertaken.

It is important to first note that the HF/6-311++G(3df,3pd) *anharmonic*  $\delta(\text{HOH})$  frequency for the free water molecule computed by SOPT is in an excellent agreement with the experimental one ( $1605.6$  vs.  $1594.6\text{ cm}^{-1}$ ). The value calculated from the potential energy parameters by the linear variation methodology ( $1596.8\text{ cm}^{-1}$ ) is in an even closer agreement with the experiment. On the other hand, the HF/LANL2DZ SOPT value is  $1570.8\text{ cm}^{-1}$ , i.e. somewhat lower than the experimental one. However, since in the present study the main emphasis was placed not on the quantitative agreement with the experimental data, but rather on the attempt to explain the mechanisms that could possibly lead to the unusually large red shift of the  $\delta(\text{HOH})$  mode in the studied series of compounds (as compared to “free” water molecule), all of the above-mentioned approaches seem promising. So, we decided to further consider these aspects more thoroughly.

An explicit inclusion of only the nearest neighbors of the water molecule within the  $\text{MgKPO}_4\cdot\text{H}_2\text{O}$  crystal at HF/LANL2DZ level of theory leads to a *blue* shift of the water bending mode – a result which is opposite to the experimental findings. Such theoretical results could indicate either an insufficient level of theory or, more probably, the predominant responsibility of the long-range (electrostatic) forces within the crystal for the spectroscopically observed situation. In order to check this assumption, the previously described finite-field study has been carried out. The application of a finite-field

with a direction *parallel* to the water dipole moment, leads to a significant flattening of the  $\delta(\text{HOH})$  potential, and consequently to a large *red shift* of this mode. For relatively low field strengths, the anharmonic effects are of a secondary importance and basically no systematic trend in the variation of the anharmonic force constants with the field are observed. However, these effects become important as the field strength increases. It is important to note at this point that the flattening of the potential is accompanied with an *increase* of the HOH angle. This result is opposite to the conclusion deduced on the basis of available spectroscopic data (see above) that the HOH angle within the  $\text{MKPO}_4 \cdot \text{H}_2\text{O}$  family of compounds is expected to be nearly  $90^\circ$ . On the other hand, the semiempirical SCF quantum methodology based on the PM3 Hamiltonian, predicts qualitatively a correct trend in the  $\delta(\text{HOH})$  frequencies even upon an inclusion of just the nearest neighbours of the water molecule within the  $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$  crystal but the predicted red shift is *too large*, and perhaps somewhat fortuitous. Within the PM3 Hamiltonian, the  $\text{Mg}^{2+}$  and  $\text{K}^+$  cations are basically represented as point charges, so the obtained results can not be considered as "explicitly including the nearest neighbors". Our further efforts will be directed towards a more systematic study of all possible factors that could lead to the spectroscopically observed situation, employing sufficiently high levels of theory, with an explicit inclusion of the dynamic electron correlation effects.

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