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VERY LOW H–O–H BENDING FREQUENCIES. VI. VIBRATIONAL SPECTRA OF CdCl₂·H₂O*

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The infrared and Raman spectra of CdCl₂·H₂O as well as those of a series of its partially deuterated analogues were recorded at room and at liquid-nitrogen temperature (RT and LNT, respectively). The combined results from the analysis of the spectra were used to assign the observed bands. In the difference IR spectrum of the compound with low deuterium content ($\approx 4\%$ D) recorded at RT, one broad band is observed at around 2590 cm⁻¹ while in the LNT spectrum two bands appear (at 2584 cm⁻¹ and 2575 cm⁻¹). The appearance in the LNT spectrum of these two bands which are due to the stretching OD modes of the isotopically isolated HDO molecules points to the existence of two crystallographically different hydrogen bonds and is in accordance with the structural data for this compound. In the LNT infrared and Raman spectra of the protiated compound, one band, at 1583 cm⁻¹, is observed in the region of the bending HOH vibrations with a frequency that is decreasing with lowering the temperature. An interesting finding related to this band is that its frequency is lower than that for the water molecule in the gas phase (1594 cm⁻¹). In the RT and LNT IR spectra, only one strong band (at 560 cm⁻¹) is observed in the region of the librations of water molecules (700 cm⁻¹ – 400 cm⁻¹).

Key words: cadmium chloride monohydrate; infrared spectra; Raman spectra

INTRODUCTION

Various types of aquahalogeno complexes have been studied in the last decades by the structural chemistry group at the Institute of Chemistry, Faculty of Natural Sciences and Mathematics in Skopje. Continuing our research in studying the vibrational spectra of aquahalogeno complexes [1–16], in this work we report the results from the analysis of the infrared and Raman spectra of the protiated cadmium chloride monohydrate (CdCl₂·H₂O) and its deuterated analogues recorded at room temperature (RT) and at the liquid nitrogen boiling temperature (LNT). To the best of our knowledge, the IR and Raman

spectra of this compound and its deuterated analogues recorded at RT and LNT have not been previously studied and reported.

The structure of CdCl₂·H₂O has been determined by single-crystal X-ray diffraction [17]. It was found to crystallize in the orthorhombic space group *Pnma* with $a = 925(2)$ pm; $b = 377.6(8)$ pm; $c = 1189(2)$ pm and four formula units in the unit cell. The crystal structure consists of *m*-symmetrical [CdCl₅(H₂O)] octahedra sharing edges to form [Cd₂Cl₁₀(H₂O)₂]_n columns along [010], the columns being connected by O–H...Cl bonds of the H₂O molecules. There is only one type of water molecules in the structure. The positions of the hydrogen atoms have not been found, but

*Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

from the surrounding of the oxygen atoms, it may be deduced that the water molecules are trigonally coordinated and oriented in the mirror planes of the structure forming two different weak and strongly bent hydrogen bonds of the O–H···Cl type to two different but symmetry related Cl atoms (Cl₁ and Cl₁') with O···Cl distances of 330(3) pm and 321(3) pm. The Cd–O distance is 232(2) pm. It should be noted here that the hydrogen bond acceptor angle Cl₁–O_w–Cl₁' is 132.6(8)° and is among the highest angles of this type found in solid hydrates [18].

EXPERIMENTAL

Synthesis of CdCl₂·H₂O and its deuterated analogues

The monohydrate of cadmium chloride used in the study was a commercial compound from Merck (Darmstadt, Germany) with a pro analysis purity. It is soluble in water, so that recrystallization was performed from water and well shaped crystals were obtained. To check its identity, an X-ray diffractogram of a powder sample was obtained and analyzed, which corresponded to the one for CdCl₂·H₂O – JCPDS (PDF-00-027-0073).

The deuterated analogues were prepared by dissolving a small amount of the protiated compound in H₂O–D₂O mixtures of appropriate composition. The crystallization of these solutions was carried out in a vacuum desiccator over silica.

Recording of spectra and X-ray diffractograms

The infrared spectra were recorded of oil suspensions in Nujol and Fluorolube using the infrared interferometer Perkin-Elmer System 2000 in the spectral range from 4000 cm⁻¹ to 370 cm⁻¹ by accumulating 32 scans with a resolution of 2 cm⁻¹ and 4 cm⁻¹. The spectra were recorded at room temperature (RT) and the liquid nitrogen boiling temperature (LNT). The low temperature measurements were made in a specially designed cell P/N 21525 (Graseby Specac). For collecting and processing the Fourier-transformed infrared spectra the software packages GRAMS ANALYST 2000 [19] and GRAMS 32 [20] were used.

The Raman spectra were recorded at room temperature using the LabRam 300 (Horiba Jobin-Yvon) micro-Raman spectrometer with a He–Ne laser (red) at 633 nm and a Nd:YAG laser (green) at 532 nm. Olympus MPlanN microscope with an

enlargement factor 50 was used for focusing the laser. The spectra were recorded in the region from 4000 to 100 cm⁻¹ by accumulation of 15–30 spectra with a resolution of 2 cm⁻¹ using a grating with 1800 lines/mm. The low temperature Raman spectra were recorded in glass capillaries using the Fourier-transform Raman spectrometer RFS 100/S (Bruker) with Nd:YAG laser excitation at 1064 nm (resolution of 2 cm⁻¹). The software packages GRAMS ANALYST 2000 [19] and GRAMS 32 [20] were used for collecting and processing the Raman spectra.

The X-ray diffractograms of powdered samples (XRPD) were obtained using a Rigaku Ultima IV diffractometer with CuKα radiation with a generator with 40 kV voltage and 40 mA current. The powdered sample was placed on a silicon sample holder and data were collected at room temperature using a D/tex detector in the 2θ region from 5 to 70° with a recording speed of 10°/min.

RESULTS AND DISCUSSION

The infrared spectra of CdCl₂·H₂O recorded in Nujol mull (N) at room temperature and at the boiling temperature of liquid nitrogen are shown in Fig. 1, and the Raman spectra recorded at RT and LNT are presented in Figure 2.

Internal vibrations of water molecules

Group theory considerations suggest that three IR and three Raman active internal vibrations of the water molecules are expected due to the existence of a static field (Table 1). If the correlation field is also taken into consideration, the number of bands would significantly increase.

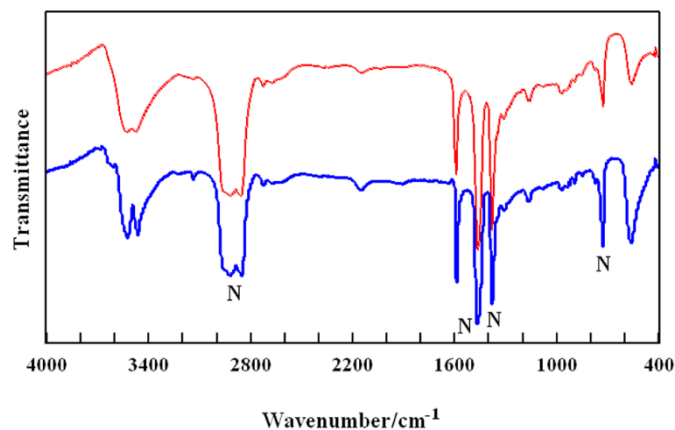


Figure 1. Infrared spectra of CdCl₂·H₂O recorded in Nujol (N) at RT (upper curve) and at LNT (lower curve).

Stretching vibrations of water molecules

In the IR spectra of CdCl₂·H₂O recorded at RT, two intensive bands, at 3525 cm⁻¹ and 3470 cm⁻¹, appear in the region of the OH stretching vibrations (Fig. 1, upper curve). In the same region, four intensive bands are observed at 3540 cm⁻¹, 3520 cm⁻¹, 3475 cm⁻¹ and 3462 cm⁻¹ in the LNT spectrum (Fig. 2, lower curve) as a result of correlation splitting of the antisymmetric and symmetric stretching HOH modes (Table 1). In the same region of the IR spectrum, one low intensity band is observed at 3133 cm⁻¹ what might be attributed to a second order transition of the bending HOH modes. In the Raman spectrum recorded at RT, the corresponding bands in this region appear at around 3470 cm⁻¹ and 3139 cm⁻¹ (Fig. 2, lower curve) whereas in the LNT spectrum, they are found at 3520 cm⁻¹, 3467 cm⁻¹ and 3130 cm⁻¹ (Fig. 2, upper curve).

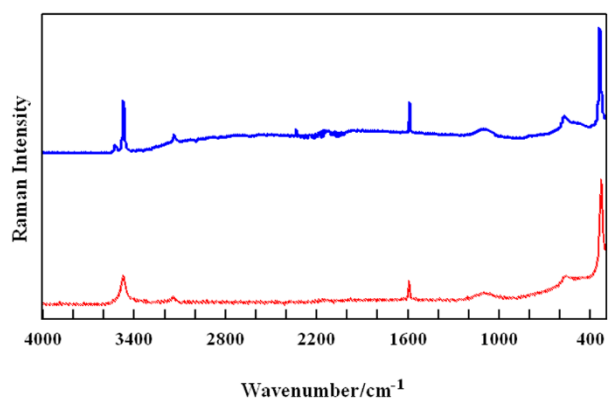


Figure 2. Raman spectra of CdCl₂·H₂O recorded at RT (lower curve) and at LNT (upper curve).

In the difference IR spectrum of the compound with low deuterium content ($\approx 4\%$ D) recorded at RT, one broad band is observed at around 2590 cm⁻¹, and two bands (at 2584 cm⁻¹ and 2575 cm⁻¹) appear in the LNT spectrum which are due to the uncoupled O–D stretching modes of isotopically isolated HDO molecules (Fig. 3). The presence of these two bands in the LNT spectrum is in accordance with the structural data of this compound [17], i.e. with the existence of two non-equivalent hydrogen bonds. The slight frequency difference between these two bands indicates that the force field for these two OD stretching vibrations is almost identical. This conclusion is strengthened by the spectral picture in the region of OD stretching modes for the series of partially deuterated analogues of the studied compound (Fig. 4). To be exact, in this region of the spectra of

the deuterated analogues, the increase of the deuterium content leads to the appearance of new bands symmetrically distributed around the two bands at 2584 cm⁻¹ and 2575 cm⁻¹. These new bands, found at 2628 cm⁻¹ and 2535 cm⁻¹, certainly originate from modes of isolated HDO molecules and can be attributed to the antisymmetric and symmetric stretching vibrations of the D₂O molecules. In the Raman spectrum of the analogue with the highest deuterium content recorded at LNT, the corresponding bands appear at 2635 cm⁻¹ and 2543 cm⁻¹, respectively (Fig. 5).

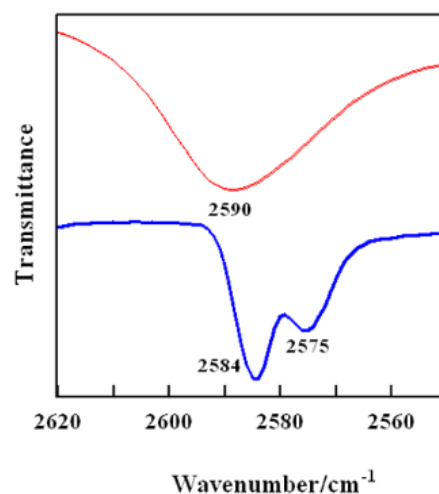


Figure 3. Deconvoluted difference infrared spectra recorded at RT (upper curve) and at LNT (lower curve) in the region of the $\nu(\text{OD})$ vibrations, obtained by subtracting the respective spectrum of the protiated sample of CdCl₂·H₂O from the spectrum of the analogue with low deuterium content ($\approx 5\%$ D).

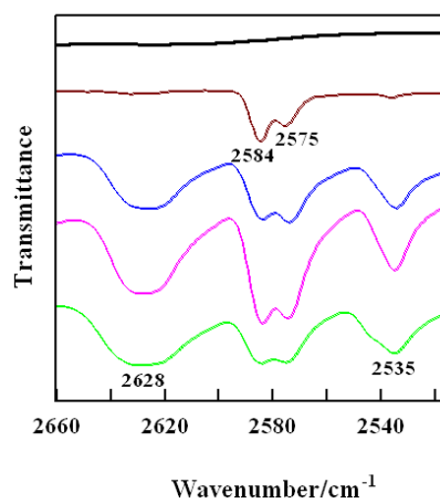
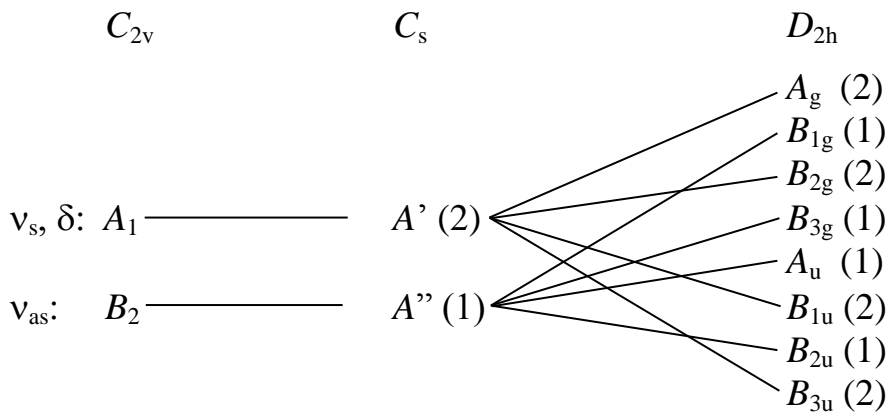


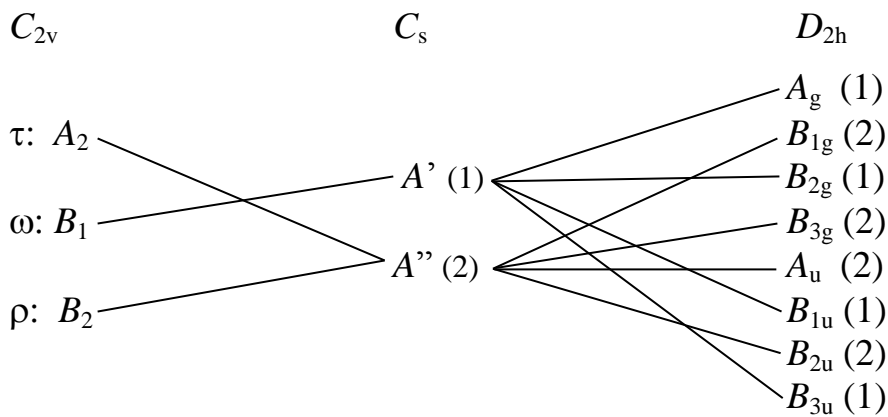
Figure 4. Infrared spectra of CdCl₂·H₂O and its partially deuterated analogues recorded at LNT in the region of the OD stretching vibrations (the content of deuterium increases from top to bottom, offset spectra are presented).

Table 1. The unit-cell group analysis for the internal and external vibrations of the water molecules in $\text{CdCl}_2 \cdot \text{H}_2\text{O}$

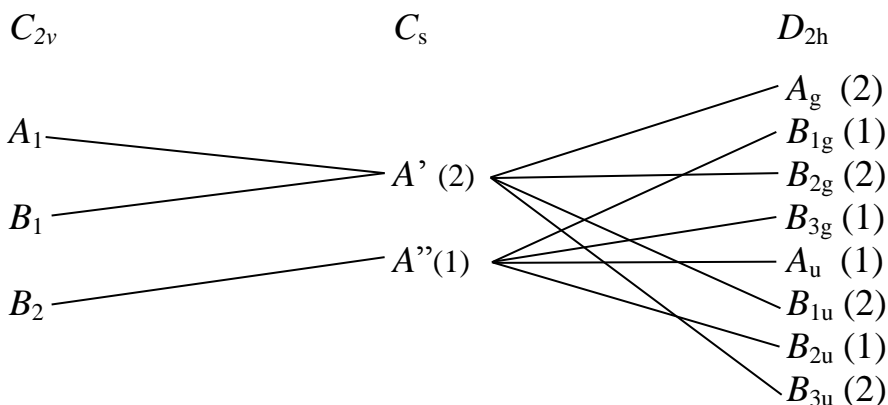
Internal vibrations



Librations



Hindered translations



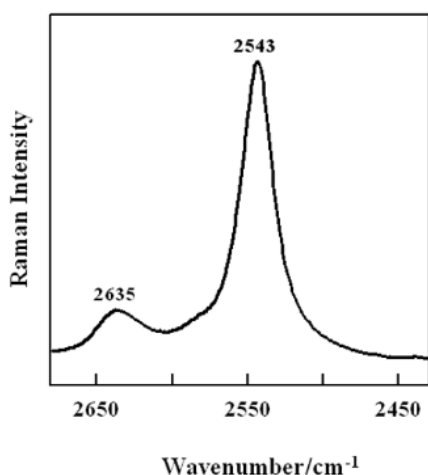


Figure 5. Raman spectrum of the nearly fully deuterated analogue of CdCl₂·H₂O recorded at LNT in the region of the OD stretching vibrations.

The temperature shift of the OD stretching mode frequencies of the isotopically isolated HDO molecules (see Fig. 3) is *positive*, i.e. $dv/dT > 0$. According to Falk et al. [21], this would point to linear hydrogen bonds. Contrary to that, the X-ray diffraction data [17], require strongly bent O–H···Cl hydrogen bonds since the hydrogen bond acceptor angle Cl₁–O_w–Cl₁' is 132.6(8)°. A similar behavior has been found for *trans*-[CrCl₂(H₂O)₄]Cl·2H₂O [12]. This means that the finding of Falk et al. [21] is not applicable in these cases.

It should be mentioned that in the case of the alkaline earth halide monohydrates MX₂·H₂O (M = Sr, Ba; X = Cl, Br, I), the temperature dependence of the OD stretching mode frequencies of isotopically isolated HDO molecules is negative ($dv/dT < 0$) [22]. In these hydrates, the water molecules are positioned in a three-dimensional [M···O···M···O]_n framework showing the same crystallographic symmetry of H₂O and its atoms as found for CdCl₂·H₂O forming also weak but this time bifurcated hydrogen bonds to the surrounding halide ions with O···Cl distances between 310.4(3) pm and 344.6(3) pm [23], i.e. the temperature dependence of the OD stretching mode frequencies of the isotopically isolated HDO molecules for the alkaline earth halide monohydrates MX₂·H₂O (M = Sr, Ba; X = Cl, Br, I) is in accordance with the finding of Falk et al. [21].

A more thorough explanation of the temperature dependence of the OD stretching mode frequencies of isotopically isolated HDO molecules of CdCl₂·H₂O and *trans*-[CrCl₂(H₂O)₄]Cl·2H₂O could be given if comparison would be made on the basis of the respective structure data determined by neutron diffraction analysis at room and low

temperature. Unfortunately, the crystal structures of these two chloride hydrates have been determined by X-ray diffraction and only at room temperature.

Bending vibrations of water molecules

The region of the bending vibrations of water molecules in the vibrational spectra is very interesting as the subtitle of the paper suggests. In the RT and LNT infrared and Raman spectra of the protiated compound (4 % D₂O, Fig. 6 a and b), one band is observed in the region of the H–O–H bending vibrations with a frequency that is decreasing with lowering the temperature.

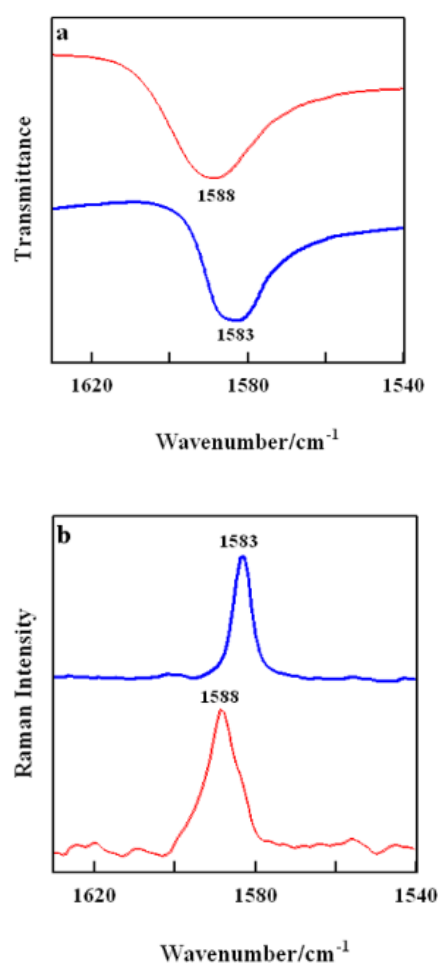


Figure 6. Infrared (a) spectrum of CdCl₂·H₂O recorded at RT (upper curve) and at LNT (lower curve) and Raman (b) spectrum of CdCl₂·H₂O recorded at RT (lower curve) and at LNT (upper curve) in the region of the HOH bending vibrations.

In the RT spectra, this band appears at 1588 cm⁻¹, and in the LNT spectra it is found at 1583 cm⁻¹. The appearance of a single band at 1583 cm⁻¹ in both the IR and Raman LNT spectra (Fig. 6

a and b) of the protiated analogue is in accordance with the existence of one crystallographically different type of water molecules in the structure. The fact that the frequencies in the two types of spectra coincide indicates an absence of the correlational splitting of modes. An interesting finding related to this band is that its frequency is lower than that for the water molecule in the gas phase, which is 1594 cm^{-1} [24], whereas in solid hydrates these frequencies are most often higher [25–27]. The appearance of the bending HOH modes at such a frequency corresponds to the existence of a very large $\text{Cl}_1\cdots\text{O}\cdots\text{Cl}_1$ angle, which is $132.6(8)^\circ$ [17]. Šoptrajanov [28, 29] has explained the differences of the frequencies of the bending vibrations between those of water molecules in the gas phase and those in solid hydrates with the respective differences of the structural features of water molecules.

In the region of the HDO and DHO bending vibrations, only one band is observed (at 1397 cm^{-1}) in the LNT IR and Raman spectra of the compound with low deuterium content instead of the expected two (Fig. 7). Similar to the case of the two OD stretching vibrations of the isotopically isolated HDO molecules, this suggests that the force fields for the HDO and DHO modes are practically identical. This means that the stretching and bending vibrations are like those of a symmetric water molecule, rather than the asymmetric one indicated by the available crystal structure data [17].

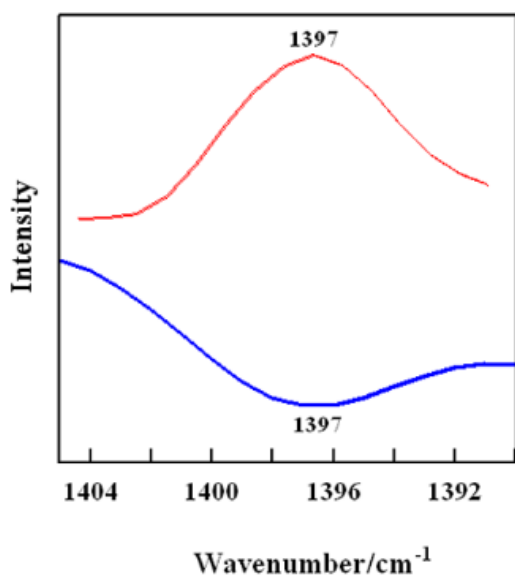


Figure 7. Infrared spectrum (lower curve) and Raman spectrum (upper curve) of $\text{CdCl}_2\cdot\text{H}_2\text{O}$ analogue with low deuterium content ($\approx 5\%$ D) recorded at LNT in the region of the HDO and DHO bending vibrations.

External vibrations of water molecules

By incorporation of the water molecules in a crystal, the rotational and translational modes of the free water molecules become vibrational modes. To distinguish these modes from the modes of free water molecules they are referred to as hindered rotations and hindered translations. Hindered rotations are also called librations and the three librational modes of water molecules are denoted as: *rocking*, *wagging* and *twisting*. Bands from librational modes in the vibrational spectra are often found in the region between 1000 cm^{-1} and 300 cm^{-1} [30]. As a rule, the bands from these modes are with higher intensity in the IR spectra than in the Raman spectra (see e.g. [31]).

Besides rotations that become librations in a crystal, the three translations of the structural units also become vibrations i.e. external vibrational modes. For coordinated water molecules, these latter vibrations have the character of metal-water modes. Hindered translations of water molecules that are not coordinated to a metal usually appear below 300 cm^{-1} , whereas for coordinated water molecules they appear in the region between 500 and 300 cm^{-1} [25].

The librational modes have been reviewed and results from systematic studies are published in the works of Falk and Knop [24], Tayal et al. [30] and Lutz [27]. In spite of the thorough studies, there are still unresolved questions related to the nature of the three librational modes, their expected frequencies, criteria for their exact assignment as well as the expected intensities of the bands from the librations of the water molecules in the IR and Raman spectra.

The librations are very sensitive to the effects related to the environment of the water molecules. Thus, changes in the structural features from one solid hydrate to another, as well as changes in temperature or isotopic substitution, have more pronounced effects on the frequency, halfwidth and intensity of the librational bands than on the bands from internal vibrations of water molecules.

The results for the vibrations of the primitive cell of the investigated compound (Table 1) show that, in absence of correlation field, the expected number of bands due to librations of water molecules in the IR and Raman spectra is three. If there is a correlation field, four bands are expected in the IR spectra and six bands due to librational HOH modes are expected in the Raman spectra.

The location of the bands from librations is facilitated by studying the isotopic $\text{H}_2\text{O}/\text{D}_2\text{O}$ and the $\text{H}_2\text{O}/\text{HDO}$ frequency shifts in the vibrational spectra [32, 33] as the following discussion will show.

In the RT and LNT IR spectra, only one strong band at 560 cm^{-1} is observed in the region of the librations of water molecules and, surprisingly, it is not temperature sensitive (Fig. 1). In the LNT Raman spectrum, one broad band with lower intensity is found at 568 cm^{-1} (Fig. 3). The appearance of only one intensive band suggests that all three librational modes (pure or mixed) have approximately the same frequency. In fact, the model calculations of Eriksson and Lindgren [34] have shown that in the case of C_s (σ_{xz} – plane) local symmetry (as is the case with cadmium chloride monohydrate), there is an intensive mixing of the *wagging* and *twisting* modes.

Considering the existence of weak hydrogen bonded water molecules, water librational bands could be expected below 400 cm^{-1} (see e.g. [30] and [35]). However, since we have studied the infrared spectra in the region only down to 400 cm^{-1} , such bands could not be observed in our infrared spectra. Thus we shall limit our discussion to bands appearing above 400 cm^{-1} .

In the LNT IR spectra of the partially deuterated analogues, new bands, not present in the spectra of the protiated compound, appear at around 480 cm^{-1} and 427 cm^{-1} with intensities increasing as the deuterium content increase (Fig. 8), the frequency factors for the $\text{H}_2\text{O}/\text{D}_2\text{O}$ and $\text{H}_2\text{O}/\text{HDO}$ isotopic shifts being 1.32 and 1.16, respectively. Such values are sufficient to assign the observed bands to librations, the higher-frequency band attributable to HDO librations and that at 425 cm^{-1} to D_2O librations.

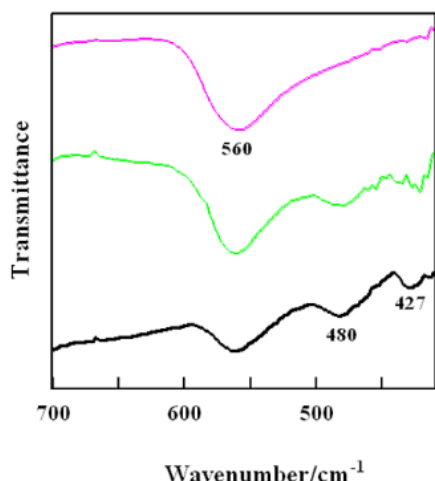


Fig. 8. IR spectra of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and its partially deuterated analogues recorded at LNT in the region of the HOH external vibrations (the content of deuterium increases from top to bottom, offset spectra are presented).

In the LNT Raman spectra of the protiated compound and the compound with the highest deuterium content (Fig. 9) bands are observed at $334/323$ and $173/164 \text{ cm}^{-1}$ (the first value refers to the protiated species and the second to the isotopomer with the highest deuterium content) that may be attributed to vibrations with a significant $\text{M-OH}_2/\text{M-OD}_2$ character, whereas the corresponding bands at 223 cm^{-1} and 205 cm^{-1} should be attributed to M-Cl modes. It is, of course, possible that some librational character could be present in the corresponding vibrational modes.

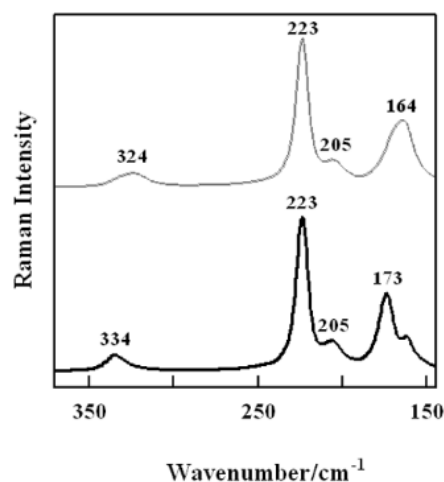


Fig. 9. Raman spectra of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (lower curve) and its almost completely deuterated analogue (upper curve) recorded at LNT in the region of the HOH external vibrations.

CONCLUSION

This paper presents a detailed interpretation of the vibrational spectra of crystalline cadmium chloride monohydrate, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, and its deuterated analogues. The analysis of the infrared and Raman spectra shows good agreement with the structural data. In the LNT infrared and Raman spectra of the protiated compound, one band, at 1583 cm^{-1} , is observed in the region of the bending HOH vibrations. An interesting finding related to this band is that its frequency is lower than that for the water molecule in the gas phase (1594 cm^{-1}), whereas in solid hydrates these frequencies are most often higher. Appearance of a band at such a low frequency in the region of HOH deformations can be correlated to the specific structural features of the water molecules in this compound.

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МНОГУ НИСКИ Н–О–Н ДЕФОРМАЦИОНИ ФРЕКВЕНЦИИ. VI. ВИБРАЦИОНИ СПЕКТРИ НА CdCl₂·H₂O

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Инфрацрвените и раманските спектри на CdCl₂·H₂O и на неговите парцијално деутерирани аналози беа снимени на собна температура и на температурата на вриење на течен азот. Севкупните резултати од анализата на спектрите беа користени за асигнација на соодветните ленти. Во диферентниот инфрацрвен спектар на соединението со ниска содржина на деутериум ($\approx 4\%$ D), снимен на собна температура, во подрачјето на валентните O–D е најдена една широка лента на околу 2590 cm⁻¹, додека во спектарот снимен на ниска температура се појавуваат две ленти (на 2584 cm⁻¹ и 2575 cm⁻¹). Појавата на овие две ленти од валентни OD модови на изотопски изолираните HDO молекули укажува на постоење на две кристалографски различни водородни врски што е во согласност со структурните податоци. Во инфрацрвените и во раманските спектри на протираното соединението снимени на ниска температура, една лента, при 1583 cm⁻¹, е најдена во областа на деформационите НОН вибрации, чија фреквенција се снижува со намалување на температурата. Интересно е што фреквенцијата на оваа вибрација е пониска од онаа на молекулата вода во гасна фаза (1594 cm⁻¹). Во инфрацрвениот спектар снимен и на собна и на ниска температура во областа на либрациите на молекулите вода (700 cm⁻¹ – 400 cm⁻¹) се појавува само една многу интензивна лента на 560 cm⁻¹.

Клучни зборови: кадмиум хлорид монохидрат; инфрацрвени спектри; рамански спектри

