

ISSN 0011-1643

UDC 543.42

CCA-2049

Original Scientific Paper

Infrared Spectra of Rubidium and Cesium Tetrachlorodiaquamanganates. I. Internal Vibrations of Water Molecules*

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Received July 17, 1991

Infrared spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and $\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ as well as those of a series of their partially deuterated analogues were recorded at room and at low temperatures (down to the liquid-nitrogen temperature).

The appearance of one single H-O-H bending band in the spectrum of the protiated compounds is in accord with the existence of one single type of water molecules in the structure of the two title compounds. On the other hand, the presence of two H-O-D bending bands in the spectra of the partially deuterated compounds is something that could be expected for water molecules situated on general positions and, thus, possessing two different protons. Finally, the existence of two O-D stretching bands in the spectra of samples with low deuterium content and of two O-H stretching bands in the spectra of the almost completely deuterated samples fits very well in the described picture.

Anharmonicity constants for the isotopically isolated water isotopomers (H_2O , HDO and D_2O) were calculated.

INTRODUCTION

Being for some time interested in the spectra of hydrates of various chlorine-containing compounds,^{1,2} we decided to study in some detail the infrared spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and $\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and of a series of their partially deuterated analogues.

The vibrational spectra of these two compounds are already partly known.

Thus, Adams and Lock³ studied the infrared and Raman spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and $\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ at room temperature (RT) and listed the frequencies of the observed bands. These authors only mentioned the existence of the observed bands in the O-H stretching region and one in the H-O-H bending region and discussed in some detail vibrations of the complex anion (including water librations).

* Dedicated to Prof. Dušan Hadži on the occasion of his 70th birthday.

Balitcheva and Pologikh⁴ made a more detailed study of the infrared spectra of the two title compounds and of their partially deuterated analogues. The degree of deuteration was not varied, however, and the spectra were apparently recorded at RT only. These authors assign the bands that are due to the stretching and bending modes of water molecules, located one water librational band and assigned the bands which originate from the metal-water stretching vibration.

The crystal structures of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and of its cesium analogue were determined by Jensen.⁵ It was concluded that the two compounds are isomorphous and crystallize in the centrosymmetric triclinic space group $P1$ with one formula unit per unit cell. However, the accuracy of the determination is rather modest, the conventional R factors for the two structures being close to 10%. Only one type of water molecules, lying on general positions, are present in the structure. They are coordinated to the manganese atoms and hydrogen-bonded to neighbouring chlorine atoms from different complex anions. The $\text{O}_w \cdots \text{Cl}$ distances are reported to be in the 317–329 pm range.

As mentioned above, we decided to reinvestigate the infrared spectra of the two title compounds and of a continuous series of their partially deuterated analogues. An attempt was made to reach a high degree of deuteration so that the O–H stretching bands of HDO molecules, isotopically isolated by D_2O molecules, could be studied. Of course, the study involved also the spectra of samples with a *low* deuterium content, in which the HDO molecules are isotopically isolated with H_2O molecules, and of samples with an average deuterium content.

Only the region of internal vibrations of water molecules will be discussed in the present communication. In a forthcoming paper,⁶ we shall present the analysis of the region where the librational and translational modes of water molecules are expected to appear.

EXPERIMENTAL

The investigated compounds were prepared using the method described in ref. 5. The deuterated analogues were prepared in a similar manner but using $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures of appropriate composition as solvents. When a high deuterium content was desired, the whole procedure was carried out in a dry box. Merck Suprapur or *p.a.* chemicals were used.

The infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer equipped with a RIIC variable temperature cell. Nujol and Fluorolube mulls and pellets with RbCl (for the rubidium compound) or CsCl (for the cesium one) were used. No significant difference was found between the spectra recorded of mulls or of pressed discs.

All spectra were recorded both at room temperature (RT) and the boiling temperature of liquid nitrogen (LNT).

RESULTS AND DISCUSSION

The infrared spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and $\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ recorded at RT and LNT between 4000 and 1000 cm^{-1} are presented in Figure 1 and Figure 2, respectively.

In order to simplify our discussion, in what follows mainly the spectra of the rubidium compound will be presented and analyzed in more detail.

The O-H and O-D Stretching Regions

As mentioned above, only one type of water molecules are present in the structure, their protons being crystallographically non-equivalent. Since there is only one formula unit in the unit cell and the two water molecules are in a *trans* position to each other around the manganese atom, which is located on an inversion centre, *two* bands are expected in the water stretching region. Two bands should be found also in the O-D stretching region of the spectra of samples with a low degree of deuteration and in the O-H stretching region of the spectra recorded from samples that are almost completely deuterated.

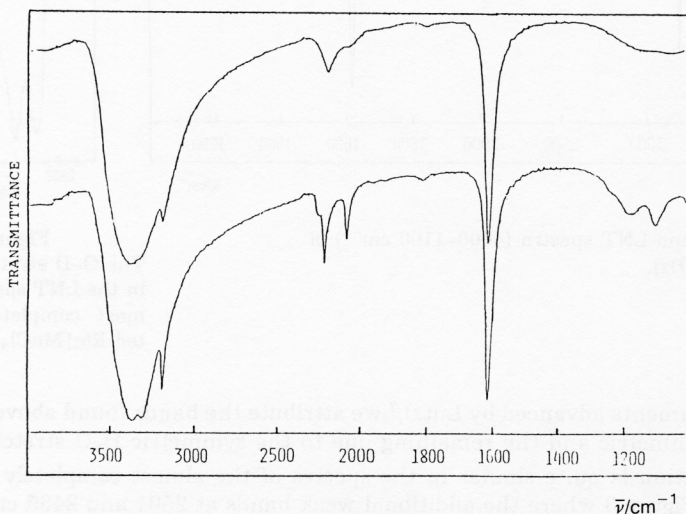


Figure 1. RT and LNT spectra ($4000\text{--}1100\text{ cm}^{-1}$) of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$.

As seen in Figures 1 and 2, contrary to the expectations, *three* bands are seen in the spectra of the two protiated compounds at both RT and LNT. The frequencies of these three bands at RT are 3400 , 3340 and 3211 cm^{-1} for $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$. The agreement with the frequencies reported by Balitcheva and Pologikh⁴ is far from being satisfactory.

At LNT, the frequencies are 3388 , 3328 and 3211 cm^{-1} for $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and 3430 , 3326 and 3210 cm^{-1} for its cesium analogue. As seen, the two highest bands in each set are temperature dependent, whereas the third one is practically insensitive to temperature changes.

Differences in the temperature behaviour of the bands indicate that they are of a different origin. Such a conclusion is supported by the significant difference in the intensity of the three bands in each set. As seen in Figure 1 and Figure 2, namely, the bands around 3210 cm^{-1} are much narrower and less intense than those at higher frequencies. It is, thus, quite safe to attribute the bands at $\approx 3210\text{ cm}^{-1}$ to second-order transitions, leaving us with the expected number of bands attributable to fundamental H_2O stretching vibrations. In agreement with the general practice (and bearing in

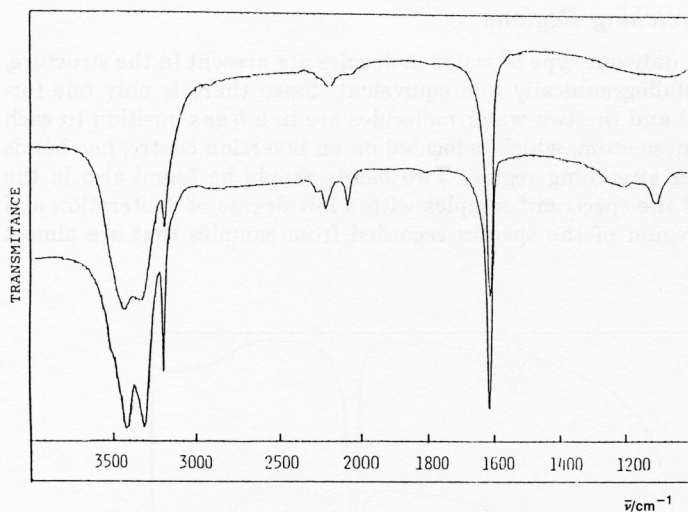


Figure 2. RT and LNT spectra (4000–1100 cm^{-1}) of $\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$.

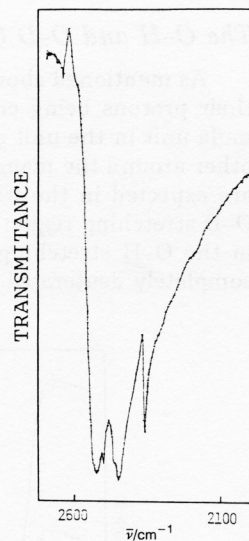


Figure 3. The O–D stretching region in the LNT spectrum of almost completely deuterated $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$.

mind the arguments advanced by Lutz),⁷ we attribute the bands found above 3350 cm^{-1} to the antisymmetric and the remaining one to the symmetric H_2O stretching mode.

The situation is quite similar in the spectra of the almost completely deuterated samples (cf. Figure 3 where the additional weak bands at 2501 and 2465 cm^{-1} are due to HDO vibrations). The frequencies of the bands in the spectra of the two studied compounds which were assigned to fundamental H_2O and D_2O stretching vibrations are summarized in Table I (together with those of the bands originating from HOH and DOD bending modes).

TABLE I

Infrared frequencies (at LNT) of the internal modes of water isotopomers in the spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and $\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$

$\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$				$\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$				Assignment
HOH	HOD	DOH	DOD	HOH	HOD	DOH	DOD	
3388	3375	3322	2523	3430	3412	3316	2542	ν_{as}
3328	2501	2465	2449	3326	2527	2461	2447	ν_{s}
3211	2847	2833	2364	3210	2853	2822	2364	2δ
1622	1433	1426	1191	1620	1437	1421	1191	δ

* The »overtones« of the bending modes are also included.

In the case of the HOD and DOH molecules, the analogues of the antisymmetric HOH stretch are almost pure O–H stretches and the analogues of the symmetric HOH stretch are almost pure O–D stretches.

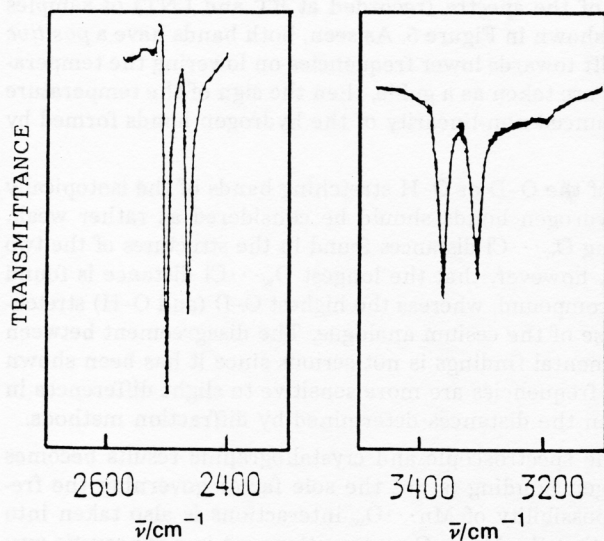


Figure 4. The O-D stretching region (a) and O-H stretching region (b) in the LNT spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ containing isotopically isolated HDO molecules.

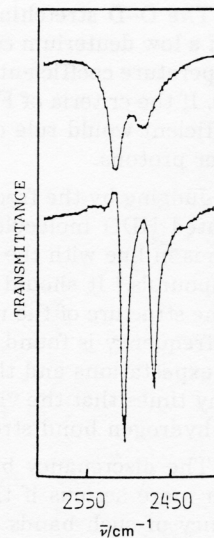


Figure 5. Comparison of the RT and LNT spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ in the O-D stretching region.

It should be noted that the differences in the temperature behaviour of the bands attributed to fundamental water stretching modes and the weaker ones interpreted as due to a second-order transition rule out the possibility of appreciable vibrational interaction between the latter mode and one of the fundamental water stretchings. The reason for this is apparently the rather large separation of the drug-energy levels. On the other hand, when the water stretching vibrations have lower frequencies (as a consequence of stronger hydrogen bonding), vibrational interactions are present, as shown for example by Othen *et al.*⁸

Frequency differences between the two H_2O stretching bands in the spectra of each of the two studied compounds deserve attention. As seen in Table I, the two bands are closer together in the case of the rubidium compounds (where the difference is approximately 60 cm^{-1}) than in the case of the cesium analogue (where it amounts to 104 cm^{-1}). The smaller frequency difference between the antisymmetric and symmetric water stretching vibrations could be taken as an indication of a smaller value for the H-O-H angle and vice versa. If this is indeed so, then it could be difficult to explain the fact that the anharmonicity constants for water bendings (see below) are practically identical for the two salts.

The picture is simpler in the O-D stretching region of the spectra of samples with a very low deuterium content and in the O-H stretching region of the spectra of almost completely deuterated samples (Figure 4). As seen, only two bands are present in both cases. These bands are clearly due to the uncoupled O-D or O-H stretches of isotopically isolated HDO molecules, their number being in agreement with the non-equivalence of the two deuterons/protons in each such molecule.

The O–D stretching region of the spectra (recorded at RT and LNT) of samples with a low deuterium content is shown in Figure 5. As seen, both bands have a *positive* temperature coefficient, *i.e.* a shift towards lower frequencies on lowering the temperature. If the criteria of Falk *et al.*⁹ are taken as a guide, then the sign of the temperature coefficient would rule out pronounced non-linearity of the hydrogen bonds formed by water protons.

Judging by the frequencies of the O–D or O–H stretching bands of the isotopically isolated HDO molecules, the hydrogen bonds should be considered as rather weak. This is in line with the rather long $O_w \cdots Cl$ distances found in the structures of the two compounds.⁵ It should be noted, however, that the longest $O_w \cdots Cl$ distance is found in the structure of the rubidium compound, whereas the highest O–D (and O–H) stretching frequency is found in the case of the cesium analogue. The disagreement between the expectations and the experimental findings is not serious since it has been shown many times that the vibrational frequencies are more sensitive to slight differences in the hydrogen bond strength than the distances determined by diffraction methods.

The discrepancy between the spectroscopic and crystallographic results becomes even more serious if the hydrogen bonding is not the sole factor governing the frequency of such bands and the possibility of $Mn \cdots O_w$ interactions is also taken into account. It has been argued,¹⁰⁻¹³ that the $Mn \cdots O_w$ interactions act in a synergetic way with hydrogen bonding in weakening the O–H (or O–D) bonds of water molecules involved in both types of interactions. Consequently, the stronger the $Mn \cdots O_w$ interactions, the larger shift towards lower frequencies is expected for the water stretching frequencies, including those of the isotopically isolated HDO molecules. The $Mn \cdots O_w$ interactions, on the other hand, are expected to be stronger for the rubidium compound (where the $Mn \cdots O_w$ distance is 208.0 pm) than for the cesium one (in this latter case,⁵ the corresponding distance is 212.8 pm).

The H–O–H, H–O–D and D–O–D Bending Region

In agreement with the expectations based on the factor-group analysis, only a single band exists in the H–O–H bending region of the spectrum of each of the two compounds (*cf.* Figures 1, 2 and 6). These bands are practically insensitive to temperature changes.

In the spectra of the partially deuterated analogues, on the other hand, two bands are seen in the H–O–D bending region (Figure 7), consistent with the presence of two non-equivalent protons in the structure. In the D–O–D bending region, a single band is again seen (Figure 8). The fact that the frequencies of the H–O–D (or D–O–H) molecules are identical, irrespective of the degree of deuteration, shows that the interactions of identical oscillators are negligible. In other words, this implies that the phonon dispersion curves are more or less straight lines.

It should be noted that the appearance of the spectra in the H–O–H bending region becomes more complicated on increasing the deuterium content in the samples (*cf.* Figure 8). The H–O–H bending band at 1621 cm^{-1} , namely, gets progressively weaker but on its high-frequency side two new bands begin to appear and gain in intensity as the deuterium content in the sample is increased. Such a picture is not difficult to explain if the existence of similar doublets of bands in the spectra of the protiated compound (Figure 1) is taken into account. The frequencies of these latter bands (2278 and 2229 cm^{-1}) are such that it is reasonable to interpret them as due to com-

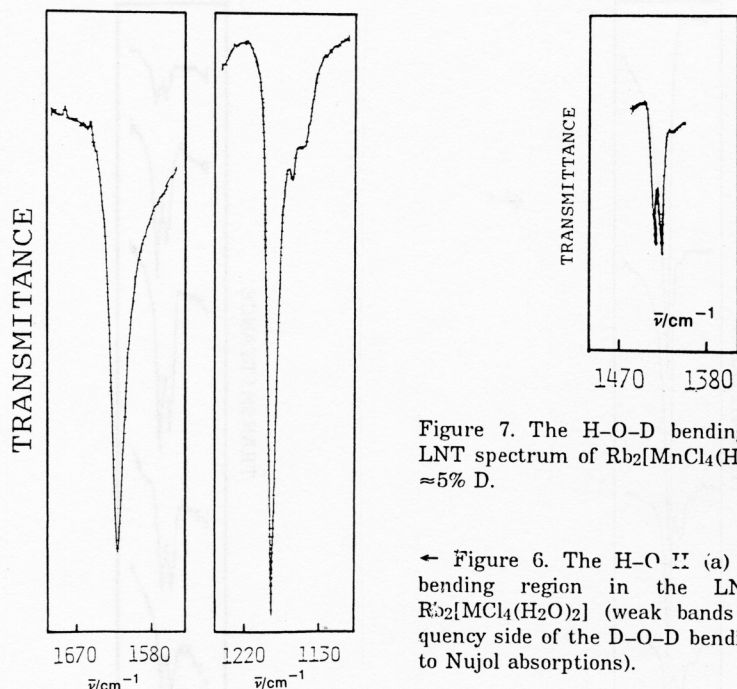


Figure 7. The H-O-D bending region in the LNT spectrum of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ containing $\approx 5\%$ D.

← Figure 6. The H-C II (a) and D-O-D (b) bending region in the LNT spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ (weak bands at the low-frequency side of the D-O-D bending band are due to Nujol absorptions).

binations of the H-O-H bending vibrations with two of the three water librations.^{6,14} A similar combination, with the remaining librational mode is responsible for the band appearing around 2100 cm^{-1} .

On the other hand, the bands seen around 1665 and 1542 cm^{-1} in the spectrum of the almost completely deuterated sample are, obviously, D_2O analogues of the bands found at 2278 and 2229 cm^{-1} .

Other Second-order Bands

The three above mentioned second-order bands are not the only ones to appear in the spectra. At 2847 and 2833 cm^{-1} in the spectra of the partially deuterated analogues of the rubidium compound, two weak bands are seen (Figure 9). These bands are interpreted as due to the »overtones« of the $\delta(\text{H-O-D})$ and $\delta(\text{D-O-H})$ modes, respectively*. Additional bands, apparently also due to second-order transitions, are seen in the region below 1200 cm^{-1} .

Anharmonicity Constants of Isotopically Isolated Water Isotopomers

As it is well known,¹⁵ the observed stretching frequencies (ν_1) of isotopically isolated HDO molecules are related to the harmonic ones ($\omega_{e,i}$), as follows:

$$\nu(\text{OH}) = \omega_e - 2\omega_e x_e$$

$$\nu(\text{OD}) = \rho\omega_e - 2\rho^2\omega_e x_e$$

*The true factor-group overtones are infrared inactive.

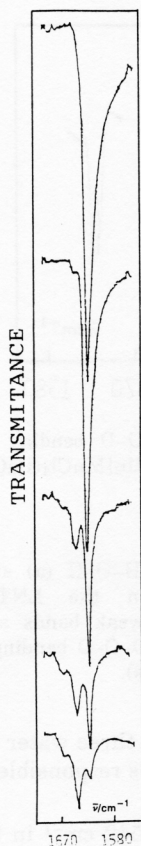


Figure 8. The H-O-H bending region in the LNT spectra of a series of partially deuterated $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ samples.

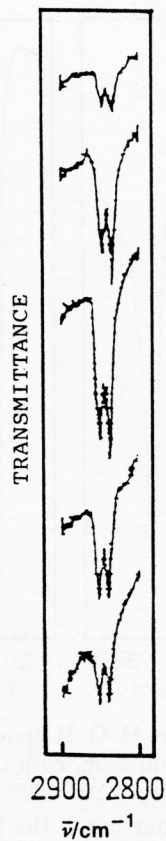


Figure 9. The 2900–2800 cm^{-1} region in the LNT spectrum of a series of partially deuterated $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ samples.

$$\omega_e = \frac{\nu(\text{OD}) - \rho^2 \nu(\text{OH})}{\rho(1 - \rho)}$$

$$\omega_e(\text{OD}) = \rho \omega_e(\text{OH})$$

where ρ is the ratio of the harmonic frequencies of the uncoupled O-D and O-H stretchings.

In order to calculate the anharmonicity constants for isotopically isolated water isotopomers, we have used the above equations, taking $\rho = 0.7257$ as found for free water molecules.¹⁶

The calculated values for the anharmonicity constants are given in Table II. As seen, values of the anharmonicity constants increase with a decrease of the O-H or O-D stretching frequencies of the isotopically isolated HDO molecules. This finding is in complete agreement with the correlations found by Berglund *et al.*¹⁷

TABLE II

Anharmonicity constants for the isotopically isolated water isotopomers*

	Rb ₂ [MnCl ₄ (H ₂ O) ₂]		Cs ₂ [MnCl ₄ (H ₂ O) ₂]	
	ν/cm^{-1}	$\omega_3\kappa_e/\text{cm}^{-1}$	ν/cm^{-1}	$\omega_e\kappa_e/\text{cm}^{-1}$
$\nu(\text{OH}_1)$	3375		3412	
$\nu(\text{OD}_1)$	2501	130.5	2527	129.0
$\nu(\text{OH}_2)$	3322		3316	
$\nu(\text{OD}_2)$	2465	137.0	2461	139.0
$\delta(\text{HOH})$	1622	16.0	1620	15.0
$\delta(\text{HOD})$	1433	9.5	1437	10.5
$\delta(\text{DOH})$	1426	9.5	1421	10.0
$\delta(\text{DOD})$	1191	9.0	1191	9.0

* HOD and DOH denote half-deuterated water molecules differing in the proton that has been isotopically substituted. H₁ and D₁ are the proton and deuteron of HOD molecules, and H₂ and D₂ are the proton and deuteron of the DOH molecules.

When calculating the anharmonicity constants for the bendings of the isotopically isolated H₂O, HDO and D₂O molecules we used the expression⁷

$$x_e\omega_e = \frac{1}{2}(2\nu_1 - \nu_2)$$

where ν_1 and ν_2 are the observed frequencies of the corresponding bonding modes and their respective »overtones«.

The values for the anharmonicity constants for the bending vibrations are also given in Table II.

Acknowledgement. – Donation of Suprapur RbCl and CaCl by E. Merck, Darmstadt, Germany, is greatly and sincerely appreciated.

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SAŽETAK

Infracrveni spektri rubidij- i cezij-tetraklorodiakvamanata. I. Unutarnje vibracije molekula vode

Viktor Stefov, Bojan Šoptrajanov i Vladimir Petruševski

Infracrveni spektri $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ i $\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$, kao i niza njihovih djelomično deuteriranih analoga snimljeni su pri sobnoj i nižim temperaturama (sve do temperature tekućeg dušika).

Pojava jedne jedine vrpce uslijed svijanja kuta H–O–H u spektru protoniranih u skladu je s postojanjem jednog tipa molekula vode u strukturi dvaju naslovnih spojeva. S druge strane, prisutnost dviju vrpca svijanja H–O–D u spektrima djelomično deuteriranih spojeva mogla se očekivati za molekule vode smještene na općim položajima, koje zato posjeduju dva različita protona. Napokon, postojanje dviju vrpca rastezanja O–D u spektrima uzoraka s niskim spektrima gotovo potpuno deuteriranih uzoraka, dobro se uklapa u opisanu sliku.

Proračunane su konstante neharmoničnosti za izotopno izolirane izotopomere vode (H_2O , HDO i D_2O).