

INFRARED SPECTRA OF RUBIDIUM AND CESIUM DIAQUATETRACHLORO- MANGANATES.

II. EXTERNAL VIBRATIONS OF THE WATER MOLECULES

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Three bands of librational origin are found in the infrared spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and of its cesium analogue. On the basis of the behaviour on partial deuteration, the band having the lowest frequency can be attributed to a mode which is essentially rocking in character. The remaining two librations are the result of the partial mixing of the twisting and wagging modes. For the HDO molecules the out-of-plane (*oop*) modes are mixed to a much higher degree, giving rise to modes which are best described as *oop* motions of the proton (H-motion) and the deuteron (D-motion) respectively.

INTRODUCTION

The infrared spectra of the simple and complex halides consist (at least in the region above 300 cm^{-1}) of bands which are due to *fundamental water modes* (internal and external vibrations) and, in many cases, to *second-order transitions* again involving water modes. Thus, the spectroscopic studies of such systems present an opportunity to study the spectrum of water with little interference of bands originating from other polyatomic groups. In a previous paper [1] we have reported our results concerning the *internal* modes of the water molecules in rubidium and cesium diaquatetrachloromanganates(2+). The present paper deals with the analysis of the bands which originate from *external* modes - hindered rotations (librations) and hindered translations (essentially metal-to-water modes).

Adams and Lock [2] reported on the vibrational (infrared and Raman) spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and of its cesium analogue recorded at room temperature (RT). The studied region extended from 4000 to 80 cm^{-1} for the infrared and from 350 to 140 cm^{-1} for the Raman spectra. The infrared spectra of the completely deuterated analogues were also reported. The bands observed from 600 to 290 cm^{-1} were attributed to water librations (wag-

ging and rocking) and to metal-water stretchings, whereas those at lower frequencies were assigned mainly to modes involving motions of the chlorine atoms. As mentioned, the infrared spectra were recorded at room temperature only and so the authors of ref. 2 could not benefit from the analysis of the low-temperature spectra (for example, those recorded at the boiling temperature of liquid nitrogen i.e. at LNT). Such spectra, on the other hand, are essential in the studies of water librations. The infrared spectra reported by Balicheva and Pologikh [3] also seem to be recorded at RT only.

A further weakness of the two sets of vibrational data reported so far [2,3] lies in the fact that the deuterium content in the samples was not varied and the possibility of assigning the water librations on the basis of their behaviour on partial deuteration was missed. It has been shown, namely (cf. [4-6] and the references quoted therein), that depending on the type of coordination, the HDO molecules may either have three more or less normal librations (for the case of tetrahedral coordination of non-distorted water molecules) or, instead, the two out-of-plane librations (wagging and twisting) may give rise to modes which are best described as out-of-plane H-motion and D-motion.

It was shown [7] that the two title compounds are isomorphous (space group $P\bar{1}$, $Z = 1$). The water molecules are trigonally coordinated (surrounded by a manganese(2+) ion and two chlorine atoms acting as proton-acceptors) and situated at sites with a C_i symmetry. The symmetry conditions are such that a complete mixing of all three librational modes is possible [4], although the coupling of the out-of-plane modes only may be more likely.

EXPERIMENTAL

Rubidium and cesium diaquatetrachloromanganate(2+) were prepared (using the method described in [7]) from aqueous solutions of rubidium (or cesium) chloride and manganese(II) chloride in stoichiometric ratios. Series of partially deuterated analogues were prepared similarly, but using as solvents H_2O/D_2O mixtures of appropriate compositions. Merck Suprapur or p.a. chemicals were used.

The infrared spectra were recorded on a Perkin-Elmer Model 580 infrared spectrophotometer. In recording the spectra, pressed disks in $RbCl$, $CsCl$ or CsI were used. The spectra of the samples with the highest deuterium content were recorded from Nujol mulls. The two sets of spectra were essentially identical. The spectra were taken both at RT and LNT but in the remaining part of this paper only the LNT spectra (as more informative) will be shown. For recording the LNT spectra, a RIIC VLT-2 cell equipped with either KBr (above 350 cm^{-1}) or polyethylene windows (down to 190 cm^{-1}) was used.

RESULTS AND DISCUSSION

The RT and LNT infrared spectra in the region between 700 and 300 cm^{-1} of the two title compounds are presented in Fig. 1.

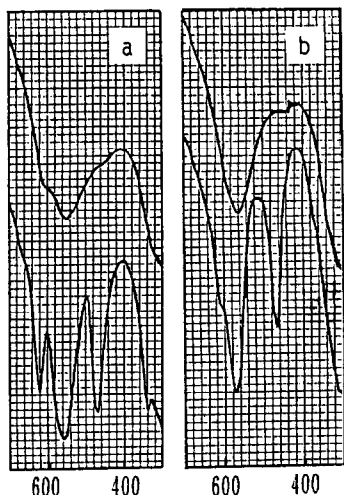


Fig. 1. The water librational region in the RT and LNT spectra of $\text{Rb}_2[\text{MnCl}_4] \cdot 2\text{H}_2\text{O}$ (a) and $\text{Cs}_2[\text{MnCl}_4] \cdot 2\text{H}_2\text{O}$ (b)

The spectra of the protiated and partially deuterated analogues in the 700 to 350 cm^{-1} region (the spectra are recorded at LNT in a cell with KBr windows) are shown in Fig. 2 a and those in the 500-190 cm^{-1} region (obtained using a cell equipped with polyethylene windows) are presented in Fig. 2 b. In all figures the deuterium content increases on going from the topmost to the bottom curve.

The agreement of our RT spectra with the data of Balicheva and Pologikh [3] is better than with those of Adams and Lock [2]. It should be pointed out that these latter authors do not even mention the existence of the very strong band found at $\approx 550 \text{ cm}^{-1}$ in the spectrum of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and list, instead, the frequencies which correspond to two weak shoulders in our spectra.

As seen in Fig. 1, three bands exist in the 650-400 cm^{-1} region of the spectrum of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$, their LNT frequencies being 622, 567 and 477 cm^{-1} (the central one is the strongest of the three). The situation is similar in the spectrum of the cesium analogue, except for the fact that a shoulder (rather than a separated band) is seen around 610 cm^{-1} . The frequencies of the remaining two bands in this case are 574 and 470 cm^{-1} . On the basis of their temperature behaviour, these bands should, beyond doubt, be attributed to water librational motions. Since the situation is clearer in the case of the rubidium compound, in what follows, reference will be made mainly to the spectra of $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ and of its partially deuterated analogues.

The comparison of the spectra presented in Fig. 2 a shows that the two highest-frequency bands continually lose intensity as the deuterium content is increased. The same seems to be true for the 477 cm^{-1} band (better visible in Fig. 2 b) although on its low-frequency side new bands appear on increasing deuterium content and this complicates the picture. The deuteration behaviour thus supports the previously made attribution of these bands to water librations.

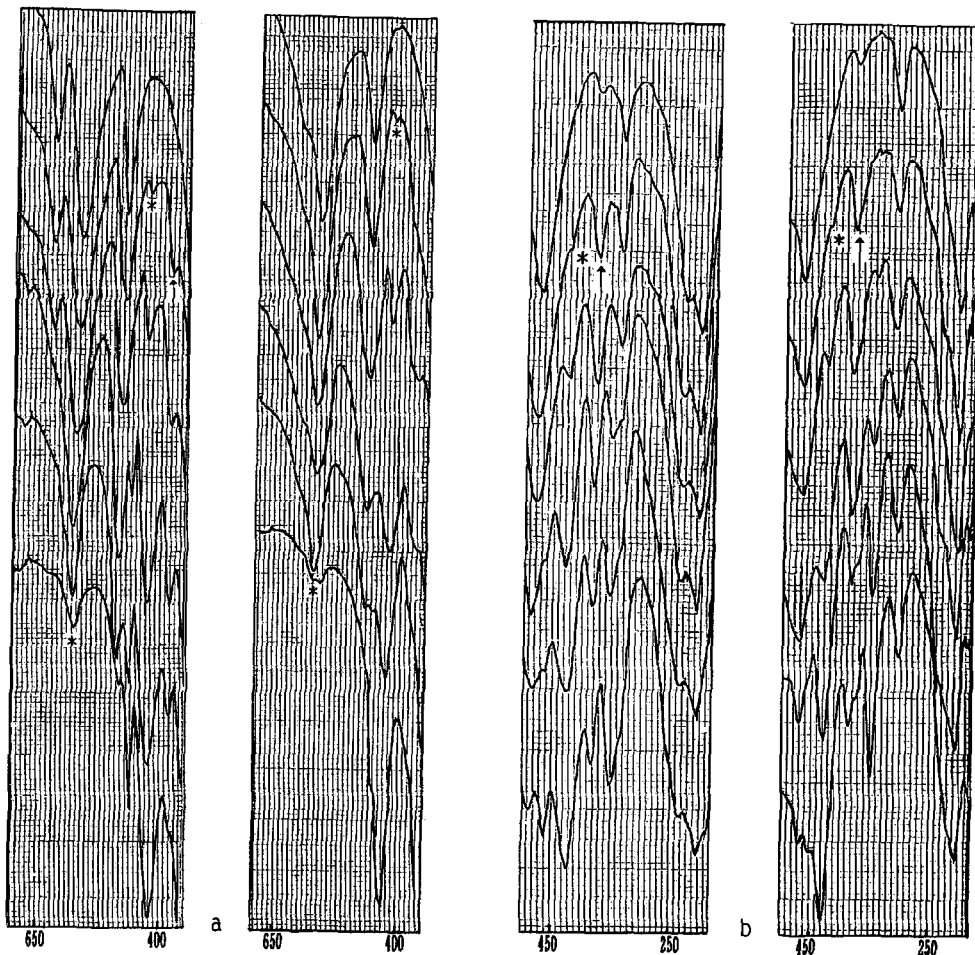


Fig. 2. The LNT spectra of series of partially deuterated analogues of $\text{Rb}_2[\text{MnCl}_4] \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2[\text{MnCl}_4] \cdot 2\text{H}_2\text{O}$ in the $700\text{--}350\text{ cm}^{-1}$ region (a) and of $\text{Rb}_2[\text{MnCl}_4] \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2[\text{MnCl}_4] \cdot 2\text{H}_2\text{O}$ in the $500\text{--}190\text{ cm}^{-1}$ region (b) (* - bands due to the H or D motions; \uparrow - rocking bands)

In the spectrum of the sample with $\approx 8\%$ deuterium, a new band appears at 381 cm^{-1} . On increasing the deuterium content in the sample, its intensity at first increases and then decreases. The deuteration behaviour of this band clearly classifies it as due to a HDO mode, most probably to the HDO rocking. If this is so, then its counterpart at 477 cm^{-1} should be assigned to the H_2O rocking libration [4]. This, then, leaves the bands at 622 and 567 cm^{-1} to be ascribed to the out-of-plane librational modes - twisting and wagging (pure or mixed)*.

* The intensity of the former band is such that it is unlikely that it could be due to pure twisting.

If the out-of-plane HDO modes are indeed essentially H-motion and D-motion, then bands are expected [4] somewhere between the frequencies of the two H₂O out-of-plane modes (H-motion) and of the two D₂O such modes (D-motion). There is no clear new band between 622 and 567 cm⁻¹, but the frequency of the band at lower frequency seems to increase on deuteration as if a superposition of the band due to the H-motion of the HDO molecules and that originating from one of the H₂O librations (almost certainly - the wagging one) were taking place. The D-motion of the HDO molecules gives rise to the band at 428 cm⁻¹, again closer to the D₂O wagging (appearing around 420 cm⁻¹) than to the twisting D₂O band (found at 461 cm⁻¹).

It should be noted that the situation found in our case is completely comparable to that encountered by Eriksson and Lindgren [8] in K₂C₂O₄·H₂O and Ba(ClO₃)₂·H₂O

The positions of the H₂O, HDO and D₂O librational bands are schematically presented in Fig. 3.

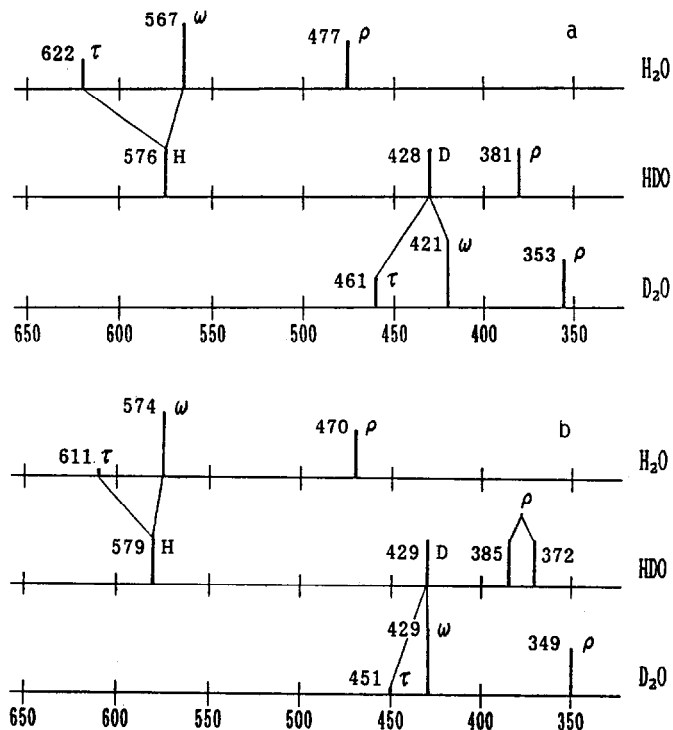


Fig. 3. Schematic representation of the position and intensity of the water librational bands in Rb₂[MnCl₄]·2H₂O (a) and Cs₂[MnCl₄]·2H₂O (b)

The band appearing at 343 cm^{-1} in the spectrum of the protiated $\text{Rb}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ could be assigned to metal-water stretching as evidenced by its small shift on deuteration (in the spectrum of the sample with the highest deuterium content, only a shoulder appears, around 334 cm^{-1} , on the side of the rocking D_2O band at 353 cm^{-1}). The ratio of the $\text{H}_2\text{O}/\text{D}_2\text{O}$ frequencies is 1.027 which is less than the theoretically expected value. In the spectra of $\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$ the slight shift of the corresponding band towards lower frequencies could be seen more clearly*. The observed value of the isotopic ratio may be taken as an indication that the corresponding mode is not a pure metal-water stretch and that other coordinates are also involved. The partner in the interaction does not seem to be the mode (essentially M-Cl stretching) giving rise to the band(s) centered around 200 cm^{-1} .

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* It appears at 315 cm^{-1} in the spectrum of the protiated and at 302 cm^{-1} in that of the deuterated $\text{Cs}_2[\text{MnCl}_4(\text{H}_2\text{O})_2]$.