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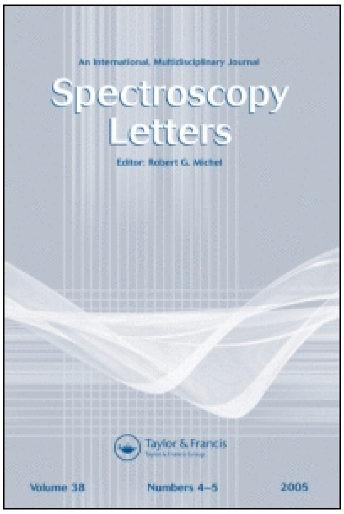

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Influence of Zn(II), Mn(II), and Mg(II) Cations on the Vibrational Spectra of Water in Aqueous Perchlorate Solutions

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INFLUENCE OF Zn(II), Mn(II), AND Mg(II) CATIONS ON THE VIBRATIONAL SPECTRA OF WATER IN AQUEOUS PERCHLORATE SOLUTIONS

KEY WORDS: aqueous solutions, divalent metal perchlorates, vibrational spectra, hydration phenomena

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ABSTRACT

Hydration of Zn(II), Mn(II), and Mg(II) perchlorates has been studied by IR and near-IR spectroscopy. Salt-affected water spectra as well as the number of salt-affected water molecules have been determined and discussed in terms of ion hydration with relation to salt concentrations.

INTRODUCTION

As nearly all natural and technical waters contain electrolytes, the progress in interpretation of water solution spectra is of great practical and theoretical importance. In spite of numerous experimental and theoretical works in the previous several decades our knowledge of this subject is still incomplete. For instance it is difficult to split the observed effect of the salt on water into cation and anion contributions. It can be done only under some rather crude and controversial assumptions.

In this work we try to obtain information about cation-water and anion-water interactions in aqueous solutions of Mn(II), Zn(II), and Mg(II) perchlorates from the analysis of the IR and near-IR vibrational spectra. It is known(1) that in these systems the cations form well defined six-coordinate first hydration shells and preserve them untouched by anions until the highest salt concentrations. It makes the interpretation of the results much easier than for other systems. The analysis of the spectra has been performed according to the procedure proposed in the previous paper(2), with the use of ν_1(OD) of HDO band, formerly measured(3), and the $2\nu_{1,3} + \nu_2$ combination band of H_2O(4,5) measured in this work for comparison purposes. Preliminary results have been partially presented at 35. Bunsen-Kolloquium in Marburg(6).

EXPERIMENTAL

$Zn(ClO_4)_2$, $Mn(ClO_4)_2$, and $Mg(ClO_4)_2$ were prepared and purified as previously(3). Absorption spectra in near-IR (1100 - 1300 nm) were measured and the computer band shape analysis has been performed as lately reported(2).

RESULTS AND DISCUSSION

The absorption spectra of aqueous Zn^{2+}, Mn^{2+}, and Mg^{2+} perchlorate solutions of the fundamental HDO vibration (IR), as well as in the range of H_2O overtone vibrations (near-IR), are rather similar. As an example the respective sets of spectra for $Zn(ClO_4)_2$

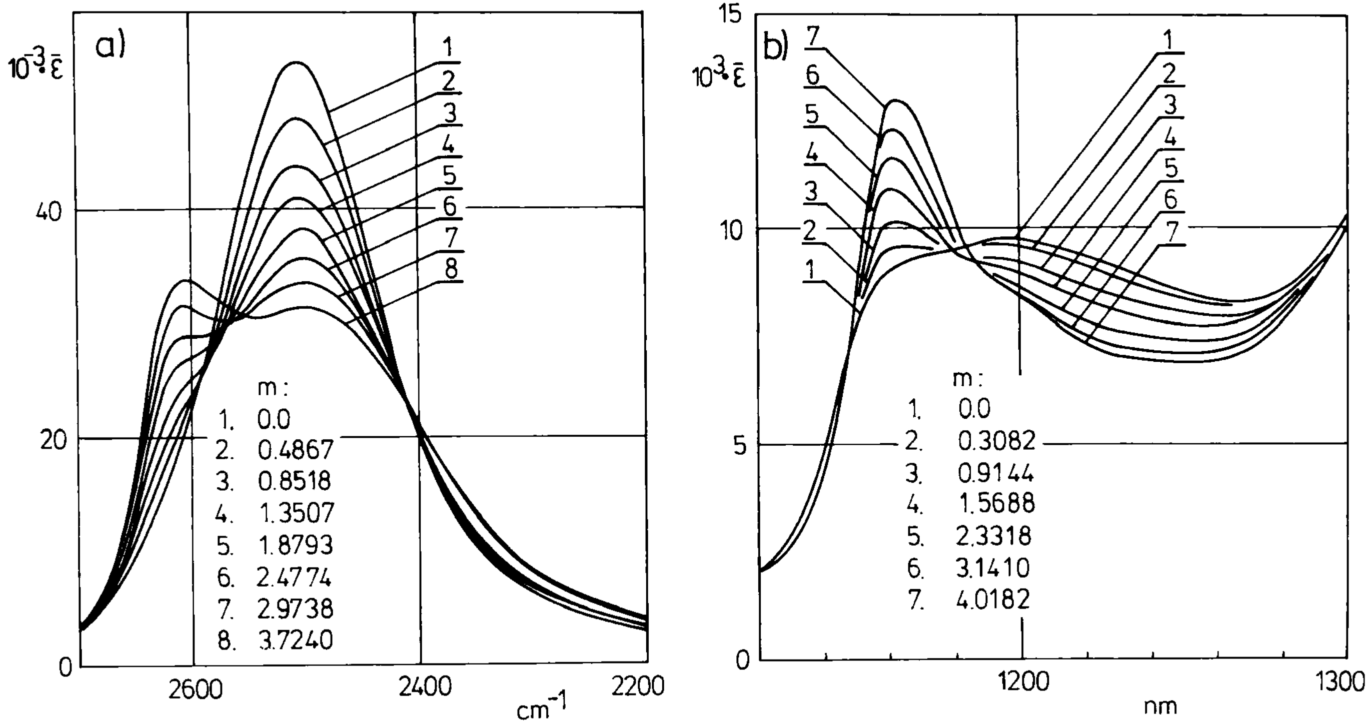
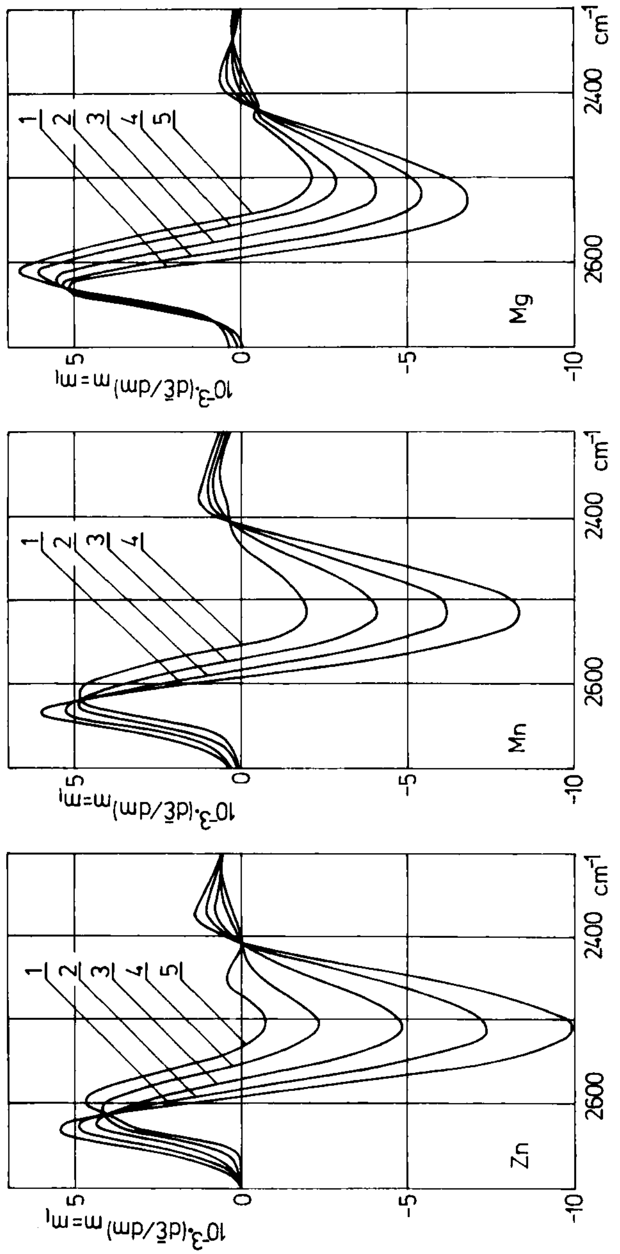


FIG. 1. Absorption spectra of water in $Zn(ClO_4)_2$ aqueous solutions at 25°C: a. for $\nu_1(OD)$ of HDO vibrations (the spectral data from Ref. 3), b. for H_2O overtone vibrations.


Zn
1
2
3
4
5
2600
2400 cm^{-1}
$10^{-3}\cdot(d\underline{\varepsilon}/dm)_{m=m_1}$
5
0
-5
-10
Mn
1
2
3
4
2600
2400 cm^{-1}
$10^{-3}\cdot(d\underline{\varepsilon}/dm)_{m=m_1}$
5
0
-5
-10
Mg
1
2
3
4
5
2600
2400 cm^{-1}
$10^{-3}\cdot(d\underline{\varepsilon}/dm)_{m=m_1}$
5
0
-5
-10

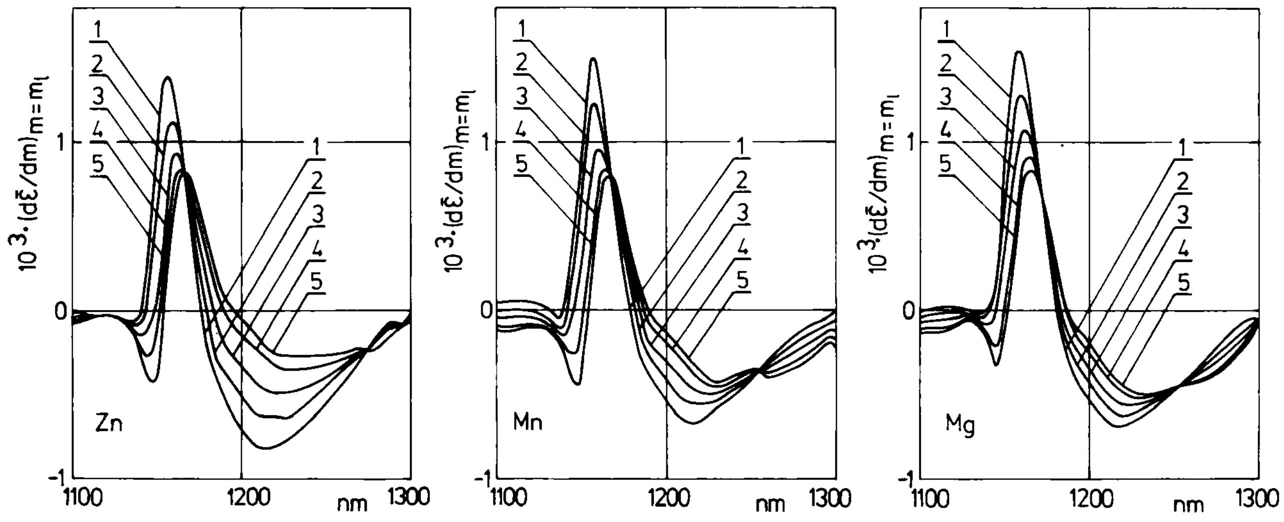


FIG. 2. The derivatives of spectral intensity vs. molality at m_1: 1, 0; 2, 1.1; 3, 2.2; 4, 3.3; 5. 4.0, for $Zn(ClO_4)_2$, $Mn(ClO_4)_2$ and $Mg(ClO_4)_2$ aqueous solutions, in the regions as in Fig. 1.

solutions are presented in Fig. 1. A more pronounced difference has been observed in the rate of the spectra intensity changes with molality, illustrated by the derivatives $(d\bar{\varepsilon}/dm)_{m = m_1}$ shown in Fig. 2. They have been determined by calculating analytic derivatives of eq.(2) at each frequency ν_i, with the use the least-squares $A(\nu_i)$ and $B(\nu_i)$ parameters of this equation. From the derivatives in Fig. 2 it is clear that spectral changes in the low-frequency part of the bands (related to the high-frequency part) are more pronounced for the fundamental than for the respective overtone bands. These discrepancies are caused by different influence of H-bonds on band intensity: the fundamental transition moment of OH oscillators strongly increases with H-bond interactions, which is accompanied by low-frequency shift, while the overtone transition moment rather slightly decreases$^{(7,8)}$.

The explanation of the observed spectral changes has been performed by determination of the respective solute-affected water spectra.

Calculations were based on eq.(1) which was derived (Ref. 2) from the assumption that water in solution might be divided into the bulk and solute-affected water$^{(9-13)}$. The fulfilment of this assumption should be the better the lower is the concentration of solution. Eq.(1) also includes the experimentally well-justified approximation$^{(2,10)}$ that the relation between mean molar absorptivity of water in solution, $\bar{\varepsilon}(\nu_i)$, and molality of the solute, m, can be fitted at every frequency, ν_i, by quadratic eq. (2). Equations (1) and (2) are presented below:

$$\varepsilon_a(\nu_i) = \frac{1}{N\cdot M}\left[A(\nu_i)\, m + B(\nu_i)\right] + \varepsilon_b(\nu_i) \qquad (1)$$

$$\bar{\varepsilon}(\nu_i) = A(\nu_i)\, m^2 + B(\nu_i)\, m + D(\nu_i) \qquad (2)$$

where $\varepsilon_a(\nu_i)$ denotes molar absorptivity of solute-affected water and $\varepsilon_b(\nu_i)$ - molar absorptivity of bulk water ($\equiv$ pure water) at the same frequency ν_i; N - the number of moles of solute-affected water per one mole of a solute, referred further as "hydration number"; M - molecular weight of water; $A(\nu_i)$, $B(\nu_i)$, and $D(\nu_i)$ - the least-squares parameters of eq.(2).

A sum of the log-normal shape functions(2,14) have been fitted to the solute-affected spectra defined by eq.(1), in which the N value has been stepwise varied. From minima on plots of the minimized function (the sum of squares of differences between the measured and calculated spectrum) vs. N the "true" hydration number, N, has been adjusted. When a minimum did not exist, the hydration number was adjusted from a run of the parameters of the log-normal component bands vs. N, see Ref. 2. Their values are shown in Table 1.

The salt-affected spectra at infinite dilution (m = 0) for the adjusted N values are shown in Figs. 3 and 4a for IR and near-IR, respectively. The spectra for both regions contain the isolated background. For IR, it may be caused by a combination band of the bending and a libration mode of H_2O(4), which appear to differ in shape in the salt solution and in pure H_2O(11) or/and may correct isolated contours of the main component bands from the pure log-normal shapes. These backgrounds and the respective cation-affected bands cannot be separated in a univocal way. For near-IR region, the background arises from another type of combination bands at about 1400 nm. In overtone spectra the high-energy band

TABLE 1

Number of salt-affected water molecules ("hydration number", N) and band positions of the ion-affected water (cm^{-1}, for HDO spectra; nm, for H_2O overtone spectra) for $Zn(ClO_4)_2$, $Mn(ClO_4)_2$, and $Mg(ClO_4)_2$ aqueous solutions

perchlorate	N	anion-affected I	cation-affected II	anion+cation-affected at m > 0 III+IV(23)
		HDO spectra		
Zn	11.5±1		2400± 7	2520±10
Mn	11 ±1	2627±2	2412±11	2530±10
Mg	10 ±1		2439± 9	2550±10
		H_2O overtone spectra		
Zn	12 ± 1		1225± 8	1210±10
Mn	10 ± 1	1158±1	1220±12	1200±10
Mg	10 ± 1		1220±12	1200±10

splits, as for $Ca(ClO_4)_2$ solutions(2), and the component at 1174±3 nm appears to be practically independent of the kind of the cation.

The spectra reveal the anion-affected (I) and cation-affected (II) water bands; their positions are listed in Table 1. The positions in IR are close to these reported by Kristiansson et al.(11) and Heinje(12). However, in contrast to the formerly cited authors(11), cation-affected band positions differ distinctly from each other and their frequences form the following order: $Zn^{2+} < Mn^{2+} < Mg^{2+}$. As Heinje(12) estimated the band position for Cu^{2+} to be 2370±20 cm^{-1}, it seems that cation-affected band shift to lower frequences for Mn-Zn transition metal cations has the Irving-Williams type plot(15), which can be justified by the ligand-field stabilization energy(16).

Because the determined N values are relatively small (Table 1), it should be supposed that they include mainly the first hydration sphere of the cation. Though N varies with the kind of cation within the limits of the estimated error, a tendency can be observed for N to increase in the same order as the cation-affected band shifts to lower frequences. Thus taking into account the cation-induced cooperativity of H-bonds, thoroughly discussed by Luck and co-workers (Ref. 13 and references cited therein), N should depend on the H-bond energy between the first and second coordination shell. Then N may include to some extent also the second coordination sphere, depending on the acidity of the aquo-cation, which should be a good measure of the ability for the formation of hydrogen bonds with molecules of second sphere(1) (the hydrolysis constants, pK, of Mg^{2+}, Mn^{2+}, and Zn^{2+} aquo-cations are equal to 11.4, 10.6, and 9.5, respectively(17)). As all these cations bind six water molecules in their first coordination zone and the minimum N value (adjusted for $Mg(ClO_4)_2$) equals to 10±1, one perchlorate anion affects not more than two water molecules. If it is true, water molecules from the nearest neighbourhood of the perchlorate anion seem to be oriented to it with both hydrogen atoms. It should be noted that this conclusion is of rather controversial character(19-21).

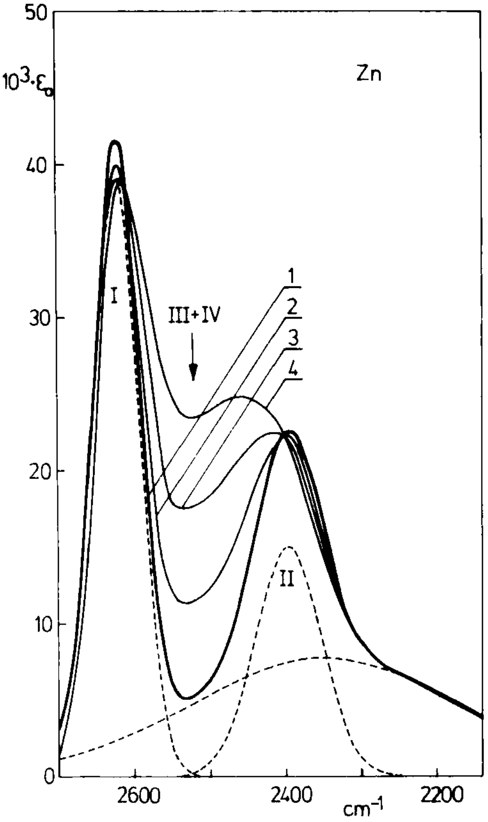


FIG. 3. Calculated salt-affected HDO spectra for $Zn(ClO_4)_2$, $Mn(ClO_4)_2$, and $Mg(ClO_4)_2$ aqueous solutions at various molalities: 1, 0; 2, 1.1; 3, 2.2; 4, 3.3. The component bands are shown for infinite dilution. I, II, III and IV denote ion-affected water bands, as in Table 1 and eq.(3).

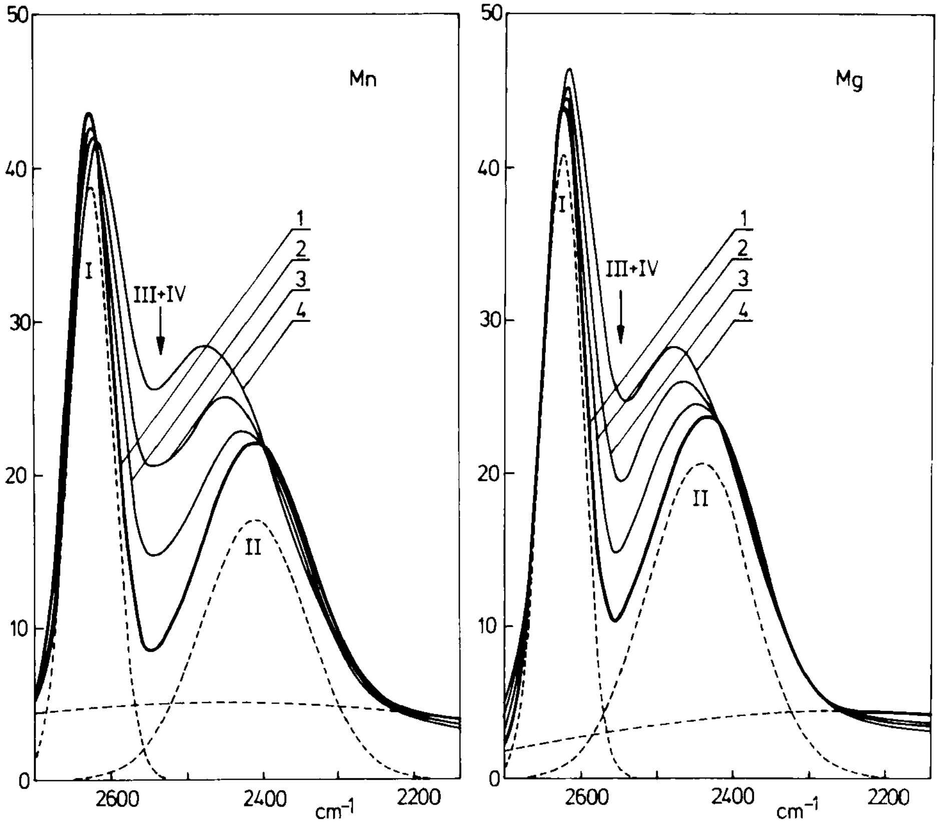


FIGURE 3 CONTINUED

In most cases a hydration number decreases with salt concentration as a result of sharing water molecules which belong to both anion and cation. This comes about in a process of inner and/or outer-sphere association of the salt(1,18). In the case of Mn-Zn transition metal and Mg perchlorates however it can be supposed that the hexacoordinate hydration sphere is preserved up to highest concentrations with probable lack of perchlorate anions in the second hydra-

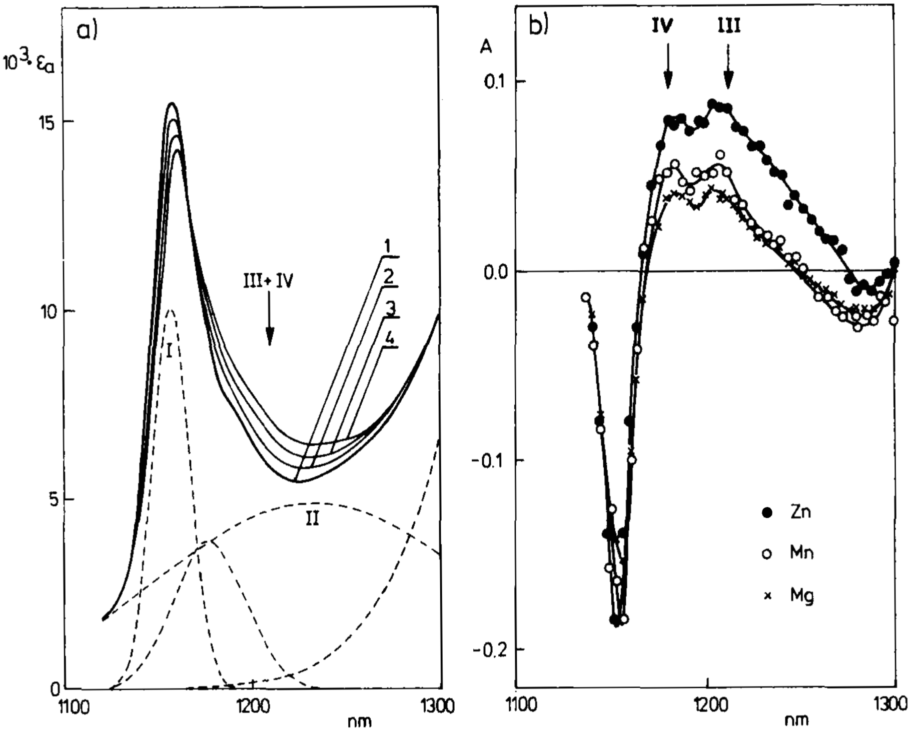


FIG. 4. a. Calculated $Zn(ClO_4)_2$-affected H_2O overtone spectra at various molalities: 1, 0; 2, 1.1; 3, 2.2; 4, 3.3. The component bands are shown for infinite dilution. b. The parameter A (see text) vs. wavelength for $Zn(ClO_4)_2$, $Mn(ClO_4)_2$, and $Mg(ClO_4)_2$ aqueous solutions. I, II, III and IV denote ion-affected water bands, as in Table 1 and eq.(3).

tion sphere in the wide range of concentrations(1). Thus, the assumption that N is independent of molality seems to be acceptable, at least for low and moderate concentrations. The salt-affected water spectra for various selected molalities (also higher), calculated on the basis of the above assumption, are presented in Figs. 3 and 4a. Intersection of respective spectra at one point is the mathematical necessity of using the quadratic eq.(2) to describe the relation between $\bar{\varepsilon}$ and m(22) and of the assumption that N is independent of m. Thus a model of a chemical equilibrium in the investigated salt-affected water systems, suggested by these "isosbestic points", may only be treated as an approximation of undergoing changes.

It can be seen in Figs. 3 and 4a that with the increase of molality a new band appears between the cationic and anionic ones, at the expense of the original bands. It seems that the new band is due to anion+cation-affected water. The order of its positions for the investigated salts is the same as it is for the respective cationic bands (Table 1). Some more detailed information of the newly formed band can be obtained from the values of parameter $A(\nu_1)$ of eq.(2). From eq.(1) it is clear that $A(\nu_1)$ values describe the changes which take place in the spectrum when the molality increases in relation to the one for an infinitely diluted solution. Plots of parameter A vs. frequency in IR, or vs. wavelength in near-IR, suggest that anion+cation-affected water bands are splitted. The respective relationships for overtone spectra are presented in Fig. 4b. A model of solution in which differently charged ions are separated by two water molecules explains these observations and is coherent with the assumption that N is independent of m. On this basis we are inclined to believe that the following approximate equilibrium takes place in the discussed metal perchlorate solutions at low and moderate concentrations:

$$\oplus\cdots\overset{\text{I}}{\boxed{\text{OD(OH)}}}\cdots H_2O \;+\; \ominus\cdots\overset{\text{II}}{\boxed{\text{OD(OH)}}} \rightleftharpoons$$

$$\oplus\cdots\overset{\text{III}}{\boxed{\text{OD(OH)}}}\cdots\overset{\text{IV}}{\boxed{\text{OD(OH)}}}\cdots\ominus \;+\; H_2O, \qquad (3)$$

where OD(OH) denotes the ion-affected OD or OH groups. With increasing salt concentration the equilibrium is shifted to the right: concentration of the I and II species decreases and the new species (III + IV) appear, in which two water molecules are trapped between cation and anion.

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22. It must be noted however that directly measured $(\bar{\varepsilon} - \varepsilon_b)/m$ values vs. ν intersect in the same ranges as least-squares $(A \cdot m + b)$ values vs. ν (see Ref. 2), within the order of the experimental error.

23. Estimated from the relation of parameter A of eq.(2) vs. frequency or wavelength (x), as the centre of gravity of area $\int_{x_1}^{x_2} A \cdot dx$ for $A \geqslant 0$ (see Fig. 4b). III and IV denote the bands of ion-affected water as in equilibrium (3).

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