Inorganic Chemistry

Article

Hydration of Oxometallate Ions in Aqueous Solution

Maciej Śmiechowski and Ingmar Persson*

Cite This: *Inorg. Chem.* 2020, 59, 8231−8239

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The strength of hydrogen bonding to and structure of hydrated oxometallate ions in aqueous solution have been studied by double difference infrared (DDIR) spectroscopy and large-angle X-ray scattering (LAXS), respectively. Anions are hydrated by accepting hydrogen bonds from the hydrating water molecules. The oxygen atom of the permanganate and perrhenate ions form weaker and longer hydrogen bonds to water than the hydrogen bonds in bulk water (i.e., they act as structure breakers), while the oxygen atoms of the chromate, dichromate, molybdate, tungstate, and hydrogenvanadate ions form hydrogen bonds stronger than those in bulk water (i.e., they act as structure makers). The oxometallate ions form one hydration shell distinguishable from bulk water as determined by DDIR spectroscopy and LAXS. The hydration of oxoanions results in X−O bond distances ca. 0.02 Å longer than those in unsolvated ions in the solid state not involved in strong bonding to counterions. The oxygens of oxoanions with a central atom from the second and third series in the periodic table and the hydrogenvanadate ion hydrogen bind three hydrating water molecules, while oxygens of oxoanions with a heavier central atom only form hydrogen bonds to two water molecules.
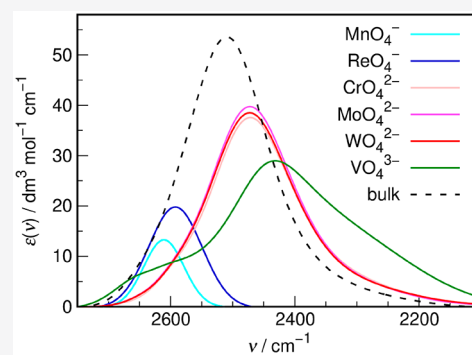
INTRODUCTION

A limited number of methods are available to study the hydration of anions in aqueous solution due to weak hydration and broad distance distribution of the hydrating water molecules. The strength of the hydrogen bonds between an anion and surrounding water molecules is preferably studied by double difference infrared (DDIR) spectroscopy.[1] Structures of hydrated anions in aqueous solution are preferably studied with large-angle X-ray and neutron scattering, LAXS[2] and LANS,[3] respectively. The most commonly applied method to study structures in solution, EXAFS, is normally not applicable as the X−(O···H−)O distance is long and the distance distribution is wide, which causes the contribution to the EXAFS function to be very small and such distances to be hardly observable.[4] Furthermore, the hydrogen atom has too weak backscattering ability to be observed accurately. However, LAXS is a very suitable method as it is very sensitive to long distances with a wide bond distance distribution according to the LAXS equation.[2] Numerous LAXS studies on aqueous solutions have been reported, while only a very limited number of LANS studies on hydrated chloride, bromide, nitrate, and perchlorate ions have been reported.[5,6]

Besides the experimental DDIR and LAXS methods, the hydration of oxoanions has been studied by computational methods. Both static quantum chemical computations and molecular dynamics (MD) simulations (based on *ab initio* electronic representation or force-field parametrization) have been applied for this purpose. Since the data on nonmetallic oxoanions have been previously reviewed and discussed in detail,[7] this summary will focus on the few computational

investigations devoted specifically to hydrated oxometallate ions.[8−11] An *ab initio* MD study on the hydrated permanganate ion in aqueous solution reports an intramolecular Mn−O bond length of 1.62 Å and four water molecules at a mean Mn(−O)···O$_{aq}$ distance of ca. 3.8 Å in a hydration shell characterized as being weak overall.[8] A detailed MD study of the hydrated chromate ion found that it is a moderate structure maker with a coordination number in water of 13−14, with every chromate oxygen forming on average 2.6 hydrogen bonds to water molecules, and a Cr−O bond length of 1.61 Å.[9] An *ab initio* MD study of aqueous tungstate revealed that WO_4^{2-} hydrolyzes easily to $[WO_n(OH)_{4-n}]^{(2-n)-}$ ions that further coordinate up to two additional water molecules in order to reach the W coordination number of 6.[10] Finally, static calculations on aqueous vanadate clusters found the intramolecular V−O bond length is 1.766 Å in hexahydrate, while the V(−O)···O$_{aq}$ distance is 2.856 Å.[11] The structure parameters and the O−D stretching frequencies measured by the DDIR method of the hydrated oxoanions in aqueous solution reported so far are summarized in Table 1.

Hydrated ions are regarded as structure makers or breakers in aqueous solution depending on their ability to form stronger or weaker hydrogen bonds, respectively, to anions or to water
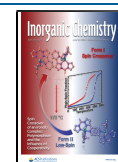
Table 1. Summary of Results from DDIR Spectroscopy and LAXS Studies of Oxoanions in Aqueous Solution

ion	$d(X-O)$/Å	$d(X-(O)\cdots O_{aq})$/Å	$d((X-)O\cdots(H-)O_{aq})$/Å	$X-O-O_{aq}$/deg	CN	$\nu(O-D)$/cm^{-1}	refs
NO_3^-	1.28	3.61	3.02	107	9	2595	12−15
ClO^-	1.662	3.85	3.045	106	3		7
ClO_2^-	1.591	3.881	3.045	110	6		16
ClO_3^-	1.501	3.770	3.021	108	9		16
ClO_4^-	1.453	3.757	3.046	109	12	2630	16
BrO_3^-	1.671	4.068	2.987	119	6		16
IO_3^-	1.829	4.27	3.013	122	6		16
IO_4^-	1.781	4.243	3.009	123	8		16
SO_3^{2-}	1.53	3.68	2.878	109	9		17
SO_4^{2-}	1.495	3.61	2.85	108	12	2477	18
$S_2O_3^{2-}$	1.479	3.622	2.854	109	12		19
SeO_3^{2-}	1.709	3.87	2.85	114	6−9	2478	20
SeO_4^{2-}	1.657	3.94	2.85	120	8	2480	20
$H_2PO_4^-$	1.527	3.711	2.85	111	12	2478	21,22
HPO_4^{2-}	1.531						21,22
PO_4^{3-}	1.533					2434	21,22
$H_2AsO_3^-$	1.785	4.096	2.85	122	6		23
AsO_3^{3-}	1.785						23
$H_2AsO_4^-$	1.707						23
$HAsO_4^{2-}$	1.704						23
AsO_4^{3-}	1.706	3.929	2.85	121	8		23
WO_4^{2-}	1.786	4.06	2.83	123	12		24
MoO_4^{2-}	1.786	4.06	2.83	123	12		24

molecules in the first hydration shell of metal ions in comparison to the intermolecular hydrogen bonds in pure water.[25] Anions with low charge density, as is the case of most monovalent ions except fluoride and hydroxide, are regarded as water structure breakers, while di- and trivalent anions are regarded as water structure makers. Previous DDIR and structural studies of hydrated anions in aqueous solution show that the O−D stretching frequency of hydrating water molecules binding to structure breaking ions is higher than that in pure water, 2510 cm^{-1}, and the $(X-)O\cdots(H)-O$ distances ($(X-)O\cdots O_{aq}$) are longer than the $O(-H)\cdots O(-H)$ distances in bulk water ($O_{aq}\cdots O_{aq}$) (Table 1). The O−D stretching frequency of the water molecules binding to structure making ions is lower than 2510 cm^{-1}, and the $(X-)O\cdots O_{aq}$ distances are shorter than 2.89 Å. The X−O, $X(-O)\cdots O_{aq}$, and $(X-)O\cdots O_{aq}$ distances are used to calculate the $X-O\cdots O_{aq}$ bond angle from which the mean number of water molecules hydrogen-bound to each oxoanion oxygen can be estimated with approximately two or three water molecules at $X-O\cdots O_{aq}$ bond angles of 120 and 109.5°, respectively. It can be observed that oxoanions with a central atom belonging to the second and third row in the periodic table bind three water molecules, while those lower in the periodic table only bind two (cf. Table 1). Whether an oxoanion hydrogen binds two or three water molecules cannot be distinguished in the O−D stretching frequencies. For example, the sulfate and selenite ions bind three and two water molecules per oxygen, respectively, but they have the same O−D stretching frequency (Table 1).

The aim of this study is to determine the hydrogen bond strength and structure parameters of the hydrated oxometallate anions in aqueous solution and to summarize the present knowledge of the hydration of anions in aqueous solution.

■ MATERIALS AND METHODS

Chemicals. Sodium permanganate monohydrate, $NaMnO_4 \cdot H_2O$ (Aldrich, 97%+), sodium perrhenate, $NaReO_4$ (Aldrich, 99.99%), sodium chromate tetrahydrate, $Na_2CrO_4 \cdot 4H_2O$ (Mallinckrodt, p.a.), sodium dichromate dihydrate, $Na_2Cr_2O_7 \cdot 2H_2O$ (Merck, p.a), sodium molybdate dihydrate, $Na_2MoO_4 \cdot 2H_2O$ (Merck, p.a.), sodium tungstate dihydrate, $Na_2WO_4 \cdot 2H_2O$ (Merck, p.a.), and sodium vanadate, Na_3VO_4 (Aldrich, 99.98%) were used as supplied. Heavy water (D_2O, 99.9% isotopic purity) was supplied by Aldrich.

Solutions. Stock solutions were prepared by dissolving amounts (weighed with 0.1 mg precision) of respective sodium salts in double-distilled water. For $NaMnO_4$, Na_2CrO_4, Na_2MoO_4, and Na_2WO_4, a series of solutions spanning the molality range ~0.2−1.0 mol·kg^{-1} were prepared by dissolving weighed amounts of the respective stock solution in double-distilled water. For the $NaReO_4$ and Na_3VO_4 salts, only the stock solutions were used for IR spectra measurement. Sample solutions containing HDO were prepared by adding 4% (by weight) of D_2O relative to H_2O and reference solutions by adding the same molar amounts of H_2O. Low fraction of D_2O is preferable, because the unfavorable equilibrium ($H_2O + D_2O \rightleftarrows 2$ HDO, $K =$ 3.86)[26] must be shifted to the right. In the present case, more than 98% of OD oscillators are found as HDO, with the additional benefit of providing a convenient raw absorbance value of ~1 in the ν_{OD} stretching vibration maximum. The final salt molalities of the HDO solutions, for which the IR spectra were collected, are reported in Table 2. The concentrations and absorption coefficients of the solutions used in the large-angle X-ray scattering measurements are

Table 2. Salt Molalities (m) of the Solutions Used for DDIR Spectroscopy Measurements

solute	m/mol kg^{-1}				
$NaMnO_4$	0.1856	0.3798	0.5926	0.7880	0.9887
$NaReO_4$	1.5567				
Na_2CrO_4	0.1888	0.3749	0.5723	0.7359	0.9315
Na_2MoO_4	0.1848	0.3698	0.5667	0.7497	0.9417
Na_2WO_4	0.1866	0.3705	0.5682	0.7602	0.9460
Na_3VO_4	0.4904				

Table 3. Compositions, pH, Densities (ρ), and Linear Absorption Coefficients (μ) of the Aqueous Sodium Permanganate, Perrhenate, Chromate, Dichromate, Molybdate, Tungstate, and Vandate Solutions Used in the LAXS Experiments

solute	$[XO_4^-]$/mol·dm^{-3}	$[Na^+]$/mol·dm^{-3}	$[H_2O]$/mol·dm^{-3}	pH	ρ/g·cm^{-3}	μ/cm^{-1}
NaMnO$_4$	1.000	1.000	52.299	12	1.0841	3.200
NaReO$_4$	1.502	1.502	51.907	12	1.3457	30.170
Na$_2$CrO$_4$	1.502	3.004	51.882	12	1.1778	3.901
Na$_2$Cr$_2$O$_7$	1.499	2.998	50.873	5	1.2692	6.341
Na$_2$MoO$_4$	1.500	3.000	52.138	12	1.201	10.057
Na$_2$WO$_4$	1.5000	3.0000	51.882	12	1.3755	28.807
Na$_3$VO$_4$	1.000	3.000	46.4494	12	1.1487	2.883

summarized in Table 3. The pH of all solutions except Na$_2$Cr$_2$O$_7$ were adjusted to pH 12 with sodium hydroxide to minimize the risk of protonation of the anion. The composition of the vanadate solution at pH 12 is dominated by the HVO$_4^{2-}$ ion, as the HVO$_4^{2-}$ ion is a very weak acid (VO$_4^{3-}$ is a strong base) with a K_{a3} value of 13.27 in dilute aqueous solution,[27] giving a composition of ca. 5% VO$_4^{3-}$ and 95% HVO$_4^{2-}$ of the studied solution. The other anions studied are much weaker bases and are not protonated at pH 12.

Instruments. *FT Infrared Spectrometer.* FTIR spectra were recorded on a PerkinElmer 1720 X spectrometer. The measurement cell was equipped with CaF$_2$ windows separated by a Teflon spacer giving a path length of 0.0026 cm, as determined interferometrically. For each spectrum, 256 scans were collected with a resolution of 4 cm^{-1} and averaged. The temperature in the instrument chamber was 26.5 ± 0.5 °C.

Large-Angle X-ray Scattering. A large-angle $\theta-\theta$ diffractometer was used to measure the scattering of Mo Kα radiation, λ = 0.7107 Å, from the free surface of the aqueous solutions. Ag Kα radiation, λ = 0.5609 Å, was used for the molybdate solution as Mo Kα radiation will cause substantial fluorescence radiation in this case. The solutions were contained in a Teflon cuvette inside a radiation shield with beryllium windows. After monochromatization of scattered radiation, by means of a focusing LiF crystal, the intensity was measured at 450 discrete points in the range of 1° < θ < 65° (the scattering angle is 2θ). A total of 100 000 counts was accumulated at each angle, and the whole angular range was scanned twice, corresponding to a statistical uncertainty of about 0.3%. The divergence of the primary X-ray beam was limited by 1 or 0.25° slits for different θ regions with overlapping some parts of the data for scaling purposes.

All data treatment was carried out using the KURVLR program[28] which has been described in detail previously.[29] The experimental intensities were normalized to a stoichiometric unit of volume containing one metal atom in the oxometallate anion, using the scattering factors f for neutral atoms, including corrections for anomalous dispersion, $\Delta f'$ and $\Delta f''$,[30] and values for Compton scattering.[31,32] For a better alignment of the intensity function, a Fourier back-transformation was applied to eliminate spurious (unrelated to any interatomic distances) peaks below 1.2 Å in the radial distribution function.[33] Least-squares refinements of the model parameters were performed by means of the STEPLR program[34] to minimize the error square sum $U = \sum w(s)[i_{exp}(s) - i_{cal}(s)]^2$.

Spectral Data Analysis. The IR spectra were analyzed by the commercial software: GRAMS/32 v. 4.01 (Galactic Industries Corporation, Salem, USA) and RAZOR (Spectrum Square Associates, Inc., Ithaca, USA) run under GRAMS/32. Spectral data were analyzed using the affected spectra method attributed to Stangret et al.,[35,36] which is conceptually similar to the one proposed independently by Lindgren and co-workers.[1,37,38] This numerical procedure leads to the separation of the spectrum of solute-affected water from the bulk water, based on all spectra in the entire solution series and of pure HDO. It has already provided a substantial library of spectral data on ionic solutes, as reviewed previously in detail.[39,40]

The procedure is based on the main assumption that water in the solution can be divided into additive contributions of solute-affected (a) and unaffected bulk (b) water: $\varepsilon c = \varepsilon_a c_a + \varepsilon_b c_b$ where ε_a and ε_b are the molar absorption coefficients (dm^3 mol^{-1} cm^{-1}) of affected and bulk water, respectively, and c symbols the respective concentrations

(mol dm^{-3}) and $c = c_a + c_b$. The length of sample cell, l, is constant in the measurements. Rearranging for ε_a, we obtain

$$\varepsilon_a = \frac{c}{c_a}(\varepsilon - \varepsilon_b) + \varepsilon_b \tag{1}$$

We now introduce the so-called "affected number", N, equal to the number of moles of water affected per mole solute. Using it and the known solute molality, m (mol kg^{-1}), the concentrations can be expressed the concentrations in eq 1 as $c = 1/MV$ and $c_a = Nm/V$, where M (kg mol^{-1}) is the mean molar mass of water in the sample (H$_2$O + 4% D$_2$O) and V (dm^3) is the volume of the solution containing m moles of solute and 1 kg of water. Substituting into eq 1 the following equation is obtained.

$$\varepsilon_a = \frac{1}{NM}\frac{\varepsilon - \varepsilon_b}{m} + \varepsilon_b \tag{2}$$

Equation 2 allows determination of the affected spectrum for a solution of finite molality provided that the N parameter is known. In this work, it is applied to the NaReO$_4$ and Na$_3$VO$_4$ solutions, for which only single stock solutions were prepared. In contrast, the advantage of using full solution series for the other solutes and an approximation of the experimental spectra ε versus m at each discrete wavenumber ν_i by the least-squares method can be performed. This makes it possible to extrapolate the spectrum of solute-affected water to the infinite dilution conditions ($m \rightarrow 0$) and eq 2 takes the form

$$\varepsilon_a = \frac{1}{NM}\left(\frac{\partial \varepsilon}{\partial m}\right)_{m=0} + \varepsilon_b \tag{3}$$

Equations 2 and 3 still contain the hitherto unknown parameter N. As mentioned above, it is formally equal to the number of moles of water spectrally affected per mole solute. It should not be directly identified with the "hydration number" or "coordination number" (in the sense of the parameters obtained from diffraction experiments or molecular simulations). N is close to the hydration number derived from direct methods only when the solute-affected HDO band differs significantly from the bulk HDO band, in either position or half-width.[36,39] Otherwise, the affected number is usually lower than the hydration number, and the solute-affected HDO spectrum carries structural and energetic information about the hydration shell in a "condensed" manner.[36]

The proper value of the affected number can be found either via a band-fitting algorithm[35,36] or chemometrically.[41,42] In this work the former method is used, which briefly consists of generating trial solute-affected water spectra for given N values and fitting them using the baseline, analytical bands, and the bulk water spectrum. A mixed Gaussian−Lorentzian product shape is used for the bands. All band parameters are kept unconstrained during the fit, with the exception of the bulk HDO spectrum, for which only intensity is allowed to vary. The maximum value of N, for which the solute-affected water spectrum still contains a negligible amount of ε_b, is considered as the "true" value of N, and the corresponding ε_a spectrum is considered the "true" affected water spectrum. The threshold value for ε_b contribution is set at ≤0.5% of the total integrated intensity of the ε_a spectrum. As a result of the fitting procedure, both unknowns (i.e., N and ε_a) are thus obtained simultaneously.

RESULTS AND DISCUSSION

Hydrogen Bonding. The final affected spectra in the ν_{OD} stretching vibrations range of HDO are shown in Figure S1. The corresponding affected numbers can be found in Table 4.

Table 4. Affected Number (N) of the Studied Sodium Salts, ν_{OD} Band Position at Maximum ($\nu°$), Full Width at Half-Height ($\Delta_{1/2}$) of the Anion-Affected HDO Spectrum after the Separation of the Na$^+$-Affected HDO Spectrum, and the Maximum Location of Intermolecular Oxygen−Oxygen Distance Distribution Obtained from the Anion-Affected HDO Spectrum ($R_{OO}°$)

solute	N	$\nu°$/cm^{-1}	$\Delta_{1/2}$/cm^{-1}	$R_{OO}°$/Å
pure HDO		2510	160	2.830
NaMnO$_4$	8.8	2610	78	2.976
NaReO$_4$	14.9	2592	103	2.968
Na$_2$CrO$_4$	15.1	2472	167	2.791
Na$_2$MoO$_4$	17.5	2472	167	2.791
Na$_2$WO$_4$	17.9	2472	167	2.791
Na$_3$VO$_4$	20.6	2432	236	2.748

As mentioned above, the affected spectra reflect the state of the solute-affected water, and the N parameter is the number of thus perturbed HDO molecules that are spectrally differentiable using the DDIR analysis.

It can immediately be seen that the spectra can be grouped into three distinct classes for monovalent, divalent, and trivalent anions, which are progressively red-shifted with increasing formal charge. This observation is in agreement with the previously found dependencies of the band position on the anion's polarizing power (q/r, where q is the ionic charge and r is the ionic radius).[23,39,40] Notably, the affected spectra for divalent oxoanions are almost identical across the entire group 6 of the periodic table.

The deconvolutions of the affected spectra into analytical bands are shown in Figures 1 and 2. The physical significance of the component bands lies in the representation of the elementary energetic states of water (HDO) underlying the more complex shape of the full spectrum. Thus, OD oscillators in different environments can be readily distinguished. Upon careful examination, these deconvolutions are seen to contain some spurious peaks (i.e., not corresponding to genuine HDO energetic states) that function as either baseline correction, atmospheric CO$_2$ absorption correction, or (in the case of Na$_3$VO$_4$) broad components of the extremely red-shifted affected ν_{OH} spectrum; this redshift is also apparent in the ν_{OD} range. Therefore, they were eliminated from further analysis,

and we proceeded with the genuine affected HDO spectra as seen in Figure 3.

The spectra in Figure 3a contain both anionic and cationic contributions. However, the influence of Na$^+$ on the HDO spectrum has been previously studied in detail.[37,39,43,44] In common with other alkali metals, it shows a slight blueshift of the ν_{OD} band to ~2540 cm^{-1} (i.e., +30 cm^{-1} from the maximum of the bulk HDO band at ~2510 cm^{-1}). The influence of the cations on the HDO spectrum was extensively reviewed previously,[39] and their effect arises primarily from modifying the solvation environment and structure of water molecules in the first hydration shell, as investigated theoretically.[45] Notably, a careful study of the affected HDO spectrum of NaPF$_6$, containing an extremely structure-breaking hexafluorophosphate anion, led to total separation of the contributions from anion and cation to the affected HDO spectrum, thus delivering an unperturbed Na$^+$-affected spectrum.[44] This was already successfully used in the extraction of the cationic contribution to ε_a in the case of NaOH.[46]

Since the affected HDO spectra for the studied oxoanions contain broad unresolved peaks that mix cationic and anionic contributions, especially in the case of divalent anions (cf. Figure 2), it is extremely difficult to ascribe the analytical component bands to genuine anionic influence. Therefore, the same procedure as that in ref 46 was applied: The separated Na$^+$-affected HDO spectrum from ref 44 was added as an analytical component to the existing fits, and the salt-affected HDO spectrum was refitted allowing only the intensity of the Na$^+$ band to vary. Finally, the converged Na$^+$ contribution was subtracted, thus providing the anion-affected HDO spectra as shown in Figure 3b. The most important parameters of these spectra are summarized in Table 2. As expected, the effect of subtraction of the Na$^+$-affected HDO spectrum depends on the overall position of the salt-affected spectrum. For the monovalent anions, for which the spectra in Figure 3a are blue-shifted with respect to that of bulk HDO, the removal of the Na$^+$ band reveals more strongly the structure-breaking character of the anion. In contrast, for the di- and trivalent anions, which are seen to red-shift the OD band position, the removal of this band induces further redshift. In any case, the elimination of the cationic influence is beneficial to a deeper understanding of the anionic part of the affected HDO spectrum.

It is informative to compare the obtained results with available data for other oxoanions. In the case of the monovalent ones, perchlorate seems to be a good reference ion. It is well-known that the ClO$_4^-$ anion is one of the more
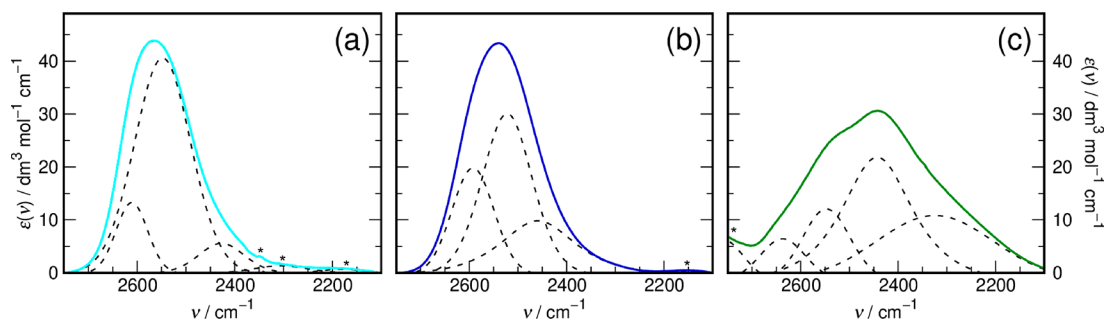

Figure 1. Deconvolution of the solute-affected spectra as shown in Figure S1 into analytical bands (dashed lines) for (a) NaMnO$_4$, (b) NaReO$_4$, and (c) Na$_3$VO$_4$. Spurious bands not belonging to the ν_{OD} vibrations of HDO are excluded from further analysis and are indicated with an asterisk.
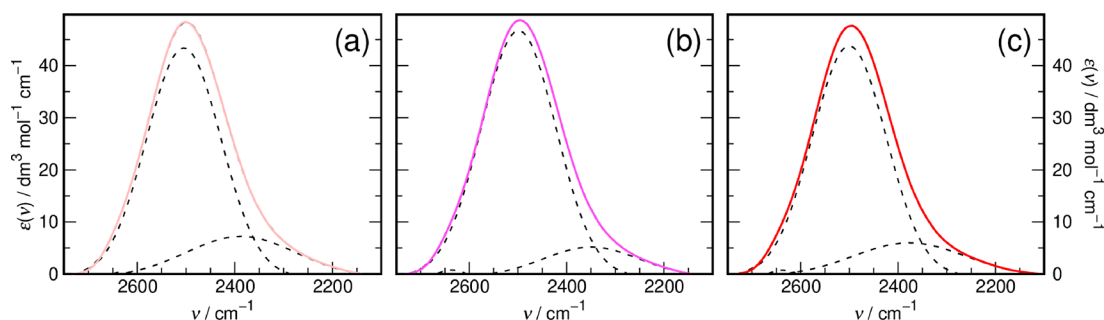
Figure 2. Deconvolution of the solute-affected spectra as shown in Figure S1 into analytical bands (dashed lines) for (a) Na_2CrO_4, (b) Na_2MoO_4, and (c) Na_2WO_4.
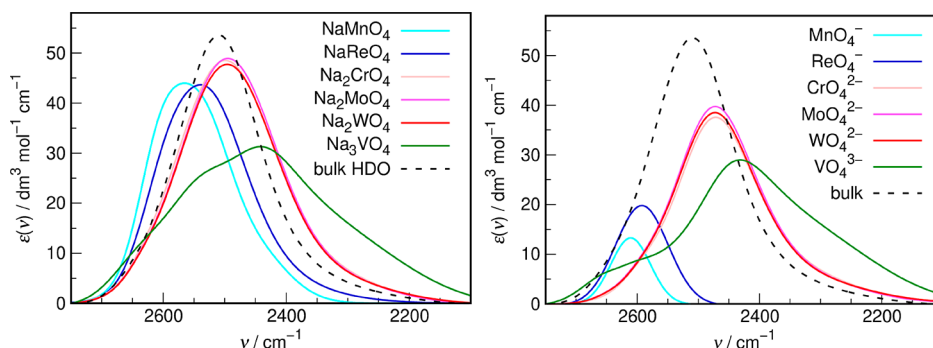

Figure 3. (a) Solute-affected spectra for the studied sodium salts in the ν_{OD} stretching vibrations range of HDO after removal of the spurious peaks compared with the bulk HDO spectrum. (b) Separated anion-affected spectra for the studied sodium salts in the ν_{OD} stretching vibrations range of HDO after removal of the Na^+-affected spectrum contribution as described in the text compared with the bulk HDO spectrum.

structure-breaking ones in aqueous solution. The maximum position of the ν_{OD} band $(\nu°)$ is ~2630 cm^{-1}.[15,35,37−39,43] Both permanganate and perrhenate are characterized with similar $\nu°$ values. Divalent and trivalent anions have been hitherto studied to a much smaller extent. However, the available limited data set corresponds well with the present results. In particular, $\nu°$ = 2477 and 2480 cm^{-1} for SO_4^{2-} and SeO_4^{2-}, respectively,[18,20] in perfect agreement with our results for the group 6 oxoanions. Similarly, $\nu°$ = 2434 cm^{-1} for PO_4^{3-},[22] the only trivalent anion studied to date, which is strikingly close to our $\nu°$ = 2432 cm^{-1} for VO_4^{3-} (see Table 4), and the affected HDO spectrum is likewise broad and contains underlying features. The full width at half-height of the anion-affected HDO spectrum increases with the increasing red shift of the ν_{OD} band. This dependence is linear to a good approximation $(\Delta_{1/2} = -0.725\nu° + 1972, R^2 = 0.91)$ and was already detected for a series of simple aqueous anions.[16] Notably, the results of the previous investigation for some particular anions are in excellent agreement with the current data, viz., $\Delta_{1/2}$ = ~75 cm^{-1} for ClO_4^-, ~170 cm^{-1} for SO_4^{2-}, and 180 cm^{-1} and for SeO_4^{2-}.[18,20]

The vanadate anion clearly stands out in the sense that the affected HDO spectrum contains underlying peaks instead of forming a single broad band resembling the bulk HDO spectrum shape. The peak positions at maximum for the three analytical bands are 2324, 2432, and 2638 cm^{-1}, in good agreement with the band parameters previously found for PO_4^{3-}.[22] On the basis of the cited work, the 2324 cm^{-1} band is ascribed to strong and short hydrogen bonds from water to the phosphate anion, while the 2432 cm^{-1} component corresponds to the hydrating waters simultaneously donating two hydrogen bonds to two oxygen atoms in VO_4^{3-}. The most blue-shifted

component band merits further investigation. At first glance, it is hard to expect severely weakened hydrogen bonds in the vicinity of a strongly hydrated ion. However, the long known concept of anticooperativity of the two hydrogen bonds donated by the same water molecule provides an explanation.[47] Namely, whenever a water molecule donates to a strong hydrogen bond, the other hydrogen is engaged in a weak hydrogen bond. This particular phenomenon has recently computationally been confirmed for PO_4^{3-}, for which the short and strong water−phosphate hydrogen bonds are accompanied by weak hydrogen bonds donated by the same hydrating water molecules to the second hydration shell.[48] While this explains the appearance of the strongly blue-shifted component band in the anion-affected HDO spectrum of VO_4^{3-}, we should mention another possible phenomenon, namely, the influence of the cation on the outermost hydration sphere of the anion detectable in the affected spectra via the formation of solvent-separated ion pairs. This was extensively discussed in the other direction (i.e., the influence of the anion on the cation's outermost hydration sphere),[44] but the same mechanism is expected to arise here. We note that the two explanations are not mutually exclusive.

A more direct comparison of HDO spectra with structural data is made possible by transforming the molar absorptivity band contour $\varepsilon_a(\nu)$ to the probability distribution of the intermolecular oxygen−oxygen distance $P(R_{OO})$. It is based on the generalization of the empirical relationship noted previously between ν_{OD}/ν_{OH} band positions of HDO in solid hydrates and the respective intermolecular distances determined by diffraction methods.[49] The details of the $\varepsilon(\nu_{OD}) \rightarrow P(R_{OO})$ transformation are published elsewhere.[36,37] In brief, it is based on the relation between R_{OO} and ν_{OD} found in solid

hydrates,[49] which is of the form $R_{OO} = [16.01 - \ln(2727 - \nu_{OD})]/3.73$. The band contour is then transformed to the probability distribution by inverting this relation and taking the derivative according to

$$P(R_{OO}) = C\varepsilon(\nu_{OD})(d\nu_{OD}/dR_{OO}) \tag{4}$$

where the normalization constant C is chosen such that the probability distribution is properly normalized to unity.

The obtained probability distributions based on the anion-affected HDO spectra are shown in Figure 4 and are compared
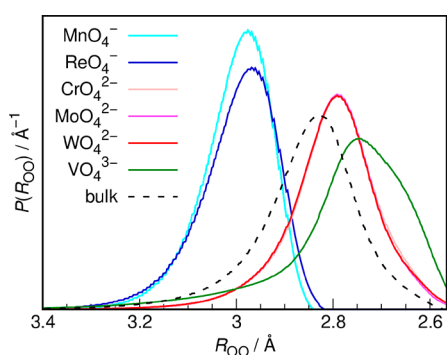

Figure 4. Intermolecular oxygen−oxygen distance distributions derived from the anion-affected HDO spectra shown in Figure 3 compared to the respective distribution in bulk HDO. The curves for the three divalent anions are almost superimposed.

with bulk water. We note that intermolecular oxygen−oxygen distance distributions for oxoanions contain contributions stemming both from anion−water and water−water (in the hydration shell) hydrogen bonds. On the basis of the data in Figure 4, we can reiterate the strongly structure breaking character of the studied monovalent anions, contrasting of the mildly structure-making divalent anions of group 6 and the more-structure-making vanadate.

Structure Determination in Aqueous Solution. The LAXS data show that the hydrated oxometallate ions bind one shell of water molecules to the oxygen atoms. The M−O and M−(O)···O$_{aq}$ distances have been determined very accurately as they are not superimposed with other distances. However, for di- and trivalent oxometallate ions, the (M−)O···O$_{aq}$ distance is too close to the bulk O$_{aq}$···O$_{aq}$ distance to be separated from each other, while for the permanganate and perrhenate ions it is sufficiently longer to be separated from of the bulk O$_{aq}$···O$_{aq}$ contribution. The mean O$_{aq}$···O$_{aq}$ distance in LAXS studies of fairly concentrated (ca. 1 mol·dm^{-3}) aqueous solution is ca. 2.89(2) Å,[2,50] while it is slightly shorter in pure water, ca. 2.85 Å.[51] For the divalent anions it was not possible to separate the O···O$_{aq}$ and O$_{aq}$···O$_{aq}$ distances, and they were refined as a mean value slightly shorter than 2.89 Å. This indicates an O···O$_{aq}$ distance of ca. 2.85 Å that has been used in the calculations of the M−O−O bond angles. All oxoanions in this study except the hydrogenvanadate hydrogen bind on average two water molecules to each oxoanion oxygen, while hydrogenvanadate ion binds three water molecules per vanadate oxygen. This is in line with previous observations that oxoanions with a central atom belonging to series 4 or higher only hydrogen bind two water molecules to each oxoanion oxygen. The hydrogenvanadate ion is the exception binding three water molecules per oxygen. The refined structure parameters of the hydrated permanganate, perrhenate,

chromate, dichromate, molybdate, tungstate, and hydrogenvanadate ions in aqueous solution as determined by LAXS are summarized in Table 5, and the fitting of the raw

Table 5. Mean Bond Distances (d), Number of Distances (N), and Temperature Coefficients (b) in the LAXS Studies of Aqueous Sodium or Lithium Oxometallate Solutions at Room Temperature[a]

species	interaction	N	d/Å	b/Å^2
	V−O	4	1.738(2)	0.0014(2)
HVO$_4^{2-}$	V−(O)···O$_{aq}$	12	3.754(4)	0.0262(7)
	V−(O···O$_{aq}$)···O$_{aq}$	24	4.323(3)	0.0390(6)
Na(H$_2$O)$_6^+$	Na−O	6	2.43(2)	0.018(2)
water bulk	O$_{aq}$···O$_{aq}$	2	2.891(3)	0.0185(5)
CrO$_4^{2-}$	Cr−O	4	1.660(3)	0.0021(2)
	Cr−(O)···O$_{aq}$	8	3.955(5)	0.0242(8)
Na(H$_2$O)$_6^+$	Na−O	6	2.432(9)	0.0187(12)
water bulk	O$_{aq}$···O$_{aq}$	2	2.886(2)	0.0174(3)
	Cr−O$_t$	2	1.616(6)	0.0019(5)
	Cr−O$_b$	2	1.806(6)	0.0029(7)
Cr$_2$O$_7^{2-}$	Cr···Cr	0.5	3.211(8)	0.0044(8)
	Cr−(O$_b$)···O$_{aq}$	4	3.72(1)	0.024(1)
	Cr−(O$_t$)···O$_{aq}$	2	3.92(1)	0.026(1)
Na(H$_2$O)$_6^+$	Na−O	6	2.42(2)	0.020(2)
water bulk	O$_{aq}$···O$_{aq}$	2	2.880(5)	0.0191(8)
MoO$_4^{2-}$	Mo−O	4	1.775(4)	0.0032(4)
	Mo−(O)···O$_{aq}$	8	4.010(3)	0.0245(4)
Li(H$_2$O)$_4^+$	Li−O	4	1.96(2)	0.010(2)
water bulk	O$_{aq}$···O$_{aq}$	2	2.881(2)	0.0202(3)
WO$_4^{2-}$	W−O	4	1.797(4)	0.0021(3)
	W−(O)···O$_{aq}$	8	4.024(4)	0.0230(5)
Na(H$_2$O)$_6^+$	Na−O	6	2.429(17)	0.0202(15)
water bulk	O$_{aq}$···O$_{aq}$	2	2.886(3)	0.0173(4)
MnO$_4^-$	Mn−O	4	1.630(5)	0.0024(5)
	Mn−(O)···O$_{aq}$	8	4.095(8)	0.0352(4)
Na(H$_2$O)$_6^+$	Na−O	6	2.428(14)	0.019(2)
water bulk	O$_{MnO4}$···O$_{aq}$	2	3.031(8)	0.038(1)
water bulk	O$_{aq}$···O$_{aq}$	2	2.889(2)	0.0212(3)
ReO$_4^-$	Re−O	4	1.735(2)	0.0022(4)
	Re−(O)···O$_{aq}$	8	4.197(7)	0.0377(4)
Na(H$_2$O)$_6^+$	Na−O	6	2.43(2)	0.018(2)
water bulk	O$_{ReO4}$···O$_{aq}$	2	3.01(4)	0.025(8)
water bulk	O$_{aq}$···O$_{aq}$	2	2.881(7)	0.0209(12)

[a]The estimated standard deviations given within parentheses include only statistical errors.

data and radial distribution function (RDF) of the sodium perrhenate solution is shown in Figure 5. The fittings of the remaining solutions are shown in Figures S2−S7.

Due to the hydration, the M−O bond distances become almost 0.02 Å longer in aqueous solution than those in solid compounds where the oxometallate anions are not binding any metal ion other than alkali metal ions or organic cations or molecules; see Tables 6 and S1. We note that the charge neutralization of the oxygens of the oxometallate anions through the hydrogen bonding of the hydrating water
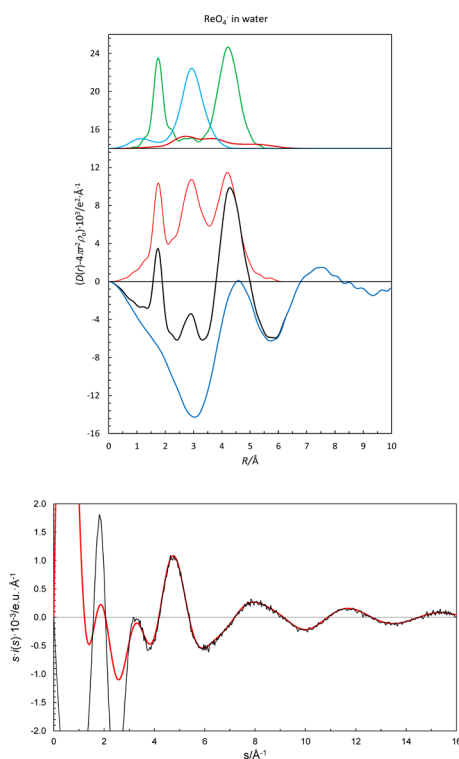
Figure 5. Top panel: LAXS radial distribution curves for a 1.502 mol·dm^{-3} aqueous solution of sodium perrhenate. (Upper part) Separate model contributions (offset: 14) of the hydrated perrhenate ion (green line), the hydrated sodium ion (brown line) and aqueous bulk (light blue line). (Middle part) Experimental RDF: $D(r) - 4\pi r^2 \rho_o$ (black line); sum of model contributions (red line); difference (blue line). Bottom panel: Reduced LAXS intensity functions $s \cdot i(s)$ (black line); model $s \cdot i_{calc}(s)$ (red line).

Table 6. Mean M−O Bond Distance in Oxometallate Anions in the Solid State (without Strong Bonds to the Oxometallate Oxygens) and Aqueous Solution[a]

	d(M−O)(s)/Å	d(M−O)(aq)/Å	diff.
VO$_4{}^{3-}$	1.720	1.738	0.018
CrO$_4{}^{2-}$	1.643	1.660	0.017
Cr$_2$O$_7{}^{2-}$	1.608 + 1.782	1.616 + 1.806	0.012 + 0.024
MoO$_4{}^{2-}$	1.756	1.775	0.019
WO$_4{}^{2-}$	1.776	1.797	0.021
MnO$_4{}^{-}$	1.611	1.630	0.019
ReO$_4{}^{-}$	1.709	1.735	0.026

[a]Tables S1 and S5, respectively.

molecules seems to be independent of the charge of the anion even though the hydrogen bond strength is different.

CONCLUSIONS

Anions are hydrated by accepting hydrogen bonds from the hydrating water molecules. Monovalent anions, except fluoride and hydroxide, form hydrogen bonds to water which are weaker and longer than the hydrogens bonds in bulk water (i.e., they act as structure breakers), while the fluoride, hydroxide, and di- and trivalent anions form hydrogen bonds stronger than those in bulk water (i.e., they act as structure makers). The anions form one hydration shell distinguishable from bulk water, as also determined by DDIR spectroscopy and LAXS. The hydration of oxoanions results in X−O bonds

ca. 0.02 Å longer than those of unsolvated ions in the solid state not involved in strong bonding to counterions as metal ions except the alkali metal ions (Tables 6 and S1). The oxygens of oxoanions with a central atom from the second and third series in the periodic table and hydrogenvanadate hydrogen bind three hydrating water molecules, while oxygens of oxoanions with a heavier central atom only hydrogen bind two water molecules (Tables 1 and 5).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00594.

Summary of metal−oxygen bond distances in reported crystal structures containing oxometallate ions not binding to a metal ion, except alkali metal ions. Double difference infrared spectra of HDO solutions of sodium oxometallates. Radial distribution functions and reduced intensity functions of the LAXS studies of the aqueous solutions of sodium permanganate, chromate, dichromate, molybdate, tungstate, and hydrogenvanadate (PDF)

AUTHOR INFORMATION

Corresponding Author

Ingmar Persson − *Department of Molecular Sciences, Swedish University of Agricultural Sciences, SE-750 07 Uppsala, Sweden;* orcid.org/0000-0002-1061-7536; Email: ingmar.persson@slu.se

Author

Maciej Śmiechowski − *Department of Physical Chemistry, Chemical Faculty, Gdańsk University of Technology, PL-80-233 Gdańsk, Poland*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c00594

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Kristiansson, O.; Eriksson, A.; Lindgren, J. Hydration of Ions in Aqueous Solutions Studied by Infrared Spectroscopy. I. Method. *Acta Chem. Scand.* **1984**, *38a*, 609−612.

(2) Johansson, G. Structures of complexes in solution derived from X-ray diffraction measurements. *Adv. Inorg. Chem.* **1992**, *39*, 159−232.

(3) Neilson, G. W. Diffraction studies of aqueous electrolyte solutions. *Pure Appl. Chem.* **1988**, *60*, 1797−1806.

(4) Teo, B. K. *EXAFS: Basic Principles and Data Analysis EXAFS*; Springer-Verlag, GmbH Co., Berlin, 2013.

(5) Ansell, S.; Barnes, A. C.; Mason, P. E.; Neilson, G. W.; Ramos, S. X-ray and neutron scattering studies of the hydration structure of alkali ions in concentrated aqueous solutions. *Biophys. Chem.* **2006**, *124*, 171−179. and references therein.

(6) Ohtaki, H.; Radnai, T. Structure and Dynamics of Hydrated Ions. *Chem. Rev.* **1993**, *93*, 1157−1204. and references therein.

(7) Eklund, L. Hydration of Oxo Anions. A Combined Computational and Experimental Structure and Dynamics Study in Aqueous Solutions. Doctoral Thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden, 2014 (available at https://pub.epsilon.slu.se/11192/).

(8) Bühl, M. Structure, Dynamics, and Magnetic Shieldings of Permanganate Ion in Aqueous Solution. A Density Functional Study. *J. Phys. Chem. A* **2002**, *106*, 10505−10509.

(9) Hinteregger, E.; Pribil, A. B.; Hofer, T. S.; Randolf, B. R.; Weiss, A. K. H.; Rode, B. M. Structure and Dynamics of the Chromate Ion in Aqueous Solution. An ab Initio QMCF-MD Simulation. *Inorg. Chem.* **2010**, *49*, 7964−7968.

(10) Rodríguez-Fortea, A.; Vilà-Nadal, L.; Poblet, J. M. Hydration of Hydrogentungstate Anions at Different pH Conditions: A Car-Parrinello Molecular Dynamics Study. *Inorg. Chem.* **2008**, *47*, 7745−7750.

(11) Pye, C. C.; Walker, V. E. J. Ab Initio Investigation of the Hydration of the Tetrahedral Perchlorate, Perbromate, Selenate, Arsenate, and Vanadate Anions. *J. Phys. Chem. A* **2011**, *115*, 13007−13015.

(12) Caminiti, R.; Cucca, P.; Radnai, T. Investigation on the Structure of Cadmium Nitrate Aqueous Solutions by X-ray Diffraction and Raman-spectroscopy. *J. Phys. Chem.* **1984**, *88*, 2382−2386.

(13) Caminiti, R.; Atzei, D.; Cucca, P.; Anedda, A.; Bongiovanni, G. Structure of Rhodium(III) Nitrate Aqueous Solutions - An Investigation by X-ray Diffraction and Raman Spectroscopy. *J. Phys. Chem.* **1986**, *90*, 238−243.

(14) Caminiti, R.; Licheri, G.; Piccaluga, G.; Pinna, G. NO_3-H_2O Interactions in aqueous-solutions. *J. Chem. Phys.* **1978**, *68*, 1967−1970.

(15) Bergström, P.-Å.; Lindgren, J.; Kristiansson, O. An IR study of the hydration of perchlorate, nitrate, iodide, bromide, chloride and sulfate anions in aqueous solution. *J. Phys. Chem.* **1991**, *95*, 8575−8580.

(16) Eklund, L.; Hofer, T. S.; Persson, I. Structure and water exchange of hydrated oxo halo ions in aqueous solution using QMCF MD simulation, large angle X-ray scattering and EXAFS. *Dalton Trans.* **2015**, *44*, 1816−1828.

(17) Eklund, L.; Hofer, T. S.; Pribil, A.; Rode, B. M.; Persson, I. On the Structure and Dynamics of the Hydrated Sulfite Ion in Aqueous Solution - An ab initio QMCF MD Simulation and Large Angle X-ray Scattering Study. *Dalton Trans.* **2012**, *41*, 5209−5216.

(18) Vchirawongkwin, V.; Rode, B. M.; Persson, I. Structure and Dynamics of Sulfate Ion in Aqueous Solution - An *ab initio* QMCF MD Simulation and Large Angle X-Ray Scattering Study. *J. Phys. Chem. B* **2007**, *111*, 4150−4155.

(19) Eklund, L.; Hofer, T. S.; Weiss, A. K. H.; Tirler, A. O.; Persson, I. Detailed structure elucidation of the hydrated thiosulfate ion using QMCF MD simulation and large angle X-ray scattering in aqueous solution. *Dalton Trans.* **2014**, *43*, 12711−12720.

(20) Eklund, L.; Persson, I. Structure and Hydrogen Bonding of the Hydrated Selenite and Selenate Ions in Aqueous Solution. *Dalton Trans.* **2014**, *43*, 6315−6321.

(21) Persson, I.; Trublet, M.; Klysubun, W. Structure Determination of Phosphoric Acid and Phosphate Ions in Aqueous Solution Using EXAFS Spectroscopy and Large Angle X-ray Scattering. *J. Phys. Chem. A* **2018**, *122*, 7413−7420.

(22) Śmiechowski, M.; Gojło, E.; Stangret, J. Systematic Study of Hydration Patterns of Phosphoric(V) Acid and Its Mono-, Di-, and Tripotassium Salts in Aqueous Solution. *J. Phys. Chem. B* **2009**, *113*, 7650−7661.

(23) Mähler, J.; Persson, I.; Herbert, R. B. Structure and Hydrogen Bonding of Arsenic Oxyacid Species in Aqueous Solution. *Dalton Trans.* **2013**, *42*, 1364−1377.

(24) Johansson, G.; Caminiti, R. The Hydration of Tungstate and Molybdate Ions in Aqueous Solution. *Z. Naturforsch., A: Phys. Sci.* **1986**, *41A*, 1325−1329.

(25) Marcus, Y. Effect of Ions on the structure of Water. Structure Making and Breaking. *Chem. Rev.* **2009**, *109*, 1346−1370.

(26) Duplan, J. C.; Mahi, L.; Brunet, J. L. NMR determination of the equilibrium constant for the liquid H_2O-D_2O mixture. *Chem. Phys. Lett.* **2005**, *413*, 400−403.

(27) Cruywagen, J. J.; Heyns, J. B. B. Vanadium(V) equilibria. Spectrophotometric and enthalpimetric investigation of the dimerization and deprotonation of HVO_4^{2-}. *Polyhedron* **1991**, *10*, 249−253.

(28) Johansson, G.; Sandström, M. Computer-programs for analysis of data on X-ray-diffraction by liquids. *Chem. Scr.* **1973**, *4*, 195−198.

(29) Stålhandske, C. M. V.; Persson, I.; Sandström, M.; Kamienska-Piotrowicz, E. A Large Angle Scattering and Vibrational Spectroscopic Study of the Solvated Zinc, Cadmium and Mercury(II) Ions in N, N-Dimethylthioformamide Solution. *Inorg. Chem.* **1997**, *36*, 3174−3182.

(30) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

(31) Cromer, D. T. Compton Scattering Factors for Aspherical Free Atoms. *J. Chem. Phys.* **1969**, *50*, 4857−4859.

(32) Cromer, D. T.; Mann, J. B. Compton Scattering Factors for Spherically Symmetric Free Atoms. *J. Chem. Phys.* **1967**, *47*, 1892−1893.

(33) Levy, H. A.; Danford, M. D.; Narten, A. H. *Data Collection and Evaluation with an X-ray Diffractometer Designed for the Study of Liquid Structure*; Technical Report ORNL-3960; Oak Ridge National Laboratory: Oak Ridge, TN, 1966.

(34) Molund, M.; Persson, I. STEPLR - A Program for Refinements of Data on X-Ray Scattering by Liquids. *Chem. Scr.* **1985**, *25*, 197−197.

(35) Stangret, J. Solute-affected vibrational-spectra of water in $Ca(ClO_4)_2$ aqueous-solutions. *Spectrosc. Lett.* **1988**, *21*, 369−381.

(36) Stangret, J.; Gampe, T. Hydration Sphere of Tetrabutylammonium Cation. FTIR Studies of HDO Spectra. *J. Phys. Chem. B* **1999**, *103*, 3778−3783.

(37) Kristiansson, O.; Eriksson, A.; Lindgren, J. Hydration of Ions in Aqueous Solutions Studied by Infrared Spectroscopy. II. Application. *Acta Chem. Scand.* **1984**, *38a*, 613−618.

(38) Kristiansson, O.; Lindgren, J.; de Villepin, J. A quantitative infrared spectroscopic method for the study of the hydration of ions in aqueous solutions. *J. Phys. Chem.* **1988**, *92*, 2680−2685.

(39) Stangret, J.; Gampe, T. Ionic Hydration Behavior Derived from Infrared Spectra of HDO. *J. Phys. Chem. A* **2002**, *106*, 5393−5402.

(40) Śmiechowski, M.; Stangret, J. Vibrational spectroscopy of semiheavy water (HDO) as a probe of solute hydration. *Pure Appl. Chem.* **2010**, *82*, 1869−1887.

(41) Bruździak, P.; Panuszko, A.; Stangret, J. Chemometric determination of solute-affected solvent vibrational spectra as a superior way of information extraction on solute solvation phenomena. *Vib. Spectrosc.* **2010**, *54*, 65−71.

(42) Bruździak, P.; Rakowska, P. W.; Stangret, J. Chemometric Method of Spectra Analysis Leading to Isolation Lysozyme and CtDNA Spectra Affected by Osmosis. *Appl. Spectrosc.* **2012**, *66*, 1302−1310.

(43) Stangret, J.; Kamieńska-Piotrowicz, E. Effect of tetraphenylphosphonium and tetraphenylborate ions on the water structure in aqueous solutions; FTIR studies of HDO spectra. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3463−3466.

(44) Gojło, E.; Śmiechowski, M.; Stangret, J. Ionic Hydration in $LiPF_6$, $NaPF_6$, and KPF_6 Aqueous Solutions Derived from Infrared HDO Spectra. *J. Phys. Chem. B* **2004**, *108*, 15938−15943.

(45) Pejov, L.; Spångberg, D.; Hermansson, K. Using MD Snapshots in ab Initio and DFT Calculations: OH Vibrations in the First Hydration Shell around $Li^+(aq)$. *J. Phys. Chem. A* **2005**, *109*, 5144−5152.

(46) Śmiechowski, M.; Stangret, J. Hydroxide Ion Hydration in Aqueous Solutions. *J. Phys. Chem. A* **2007**, *111*, 2889−2897.

(47) Luck, W. A. P.; Klein, D.; Rangsriwatananon, K. Anti-cooperativity of the two water OH groups. *J. Mol. Struct.* **1997**, *416*, 287−296.

(48) Sharma, B.; Chandra, A. Ab Initio Molecular Dynamics Simulation of the Phosphate Ion in Water: Insights into Solvation Shell Structure, Dynamics, and Kosmotropic Activity. *J. Phys. Chem. B* **2017**, *121*, 10519−10529.

(49) Berglund, B.; Lindgren, J.; Tegenfeldt, J. On the correlation between deuteron quadrupole coupling constants, O-H and O-D stretching frequencies and hydrogen-bond distances in solid hydrates. *J. Mol. Struct.* **1978**, *43*, 179−191.

(50) Jalilehvand, F.; Spångberg, D.; Lindqvist-Reis, P.; Hermansson, K.; Persson, I.; Sandström, M. Hydration of the Calcium Ion. An EXAFS, Large Angle X-ray Scattering and Molecular Dynamics Simulation Study. *J. Am. Chem. Soc.* **2001**, *123*, 431−441.

(51) Nilsson, A.; Pettersson, L. G. M. Perspective on the structure of liquid water. *Chem. Phys.* **2011**, *389*, 1−34.