Ionic Hydration in LiPF₆, NaPF₆, and KPF₆ Aqueous Solutions Derived from Infrared HDO Spectra

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Hydration of KPF_6, $NaPF_6$, and $LiPF_6$ has been studied in aqueous solutions by means of FTIR spectra of HDO isotopically diluted in H_2O. The difference spectra procedure has been applied, which allowed removal of the contribution of bulk water and thus separation of the spectra of solute-affected HDO. In all cases, a high-wavenumber component band at 2667 cm⁻¹ is present that corresponds to HDO affected by the PF_6^- anion, which is known as an extreme structure breaker. The band at ca. 2540 cm⁻¹ corresponds to HDO affected by all studied cations, and another component band at ca. 2445 cm⁻¹ is additionally visible in the case of the Li^+ cation. The probability distribution functions of interatomic O···O distances for HDO affected by the cations clearly display a lower-distance structure for Li^+, contrary to both other cations. The existence of a band situated at 2630 cm⁻¹ for each of the salts is also significant. Its previous interpretation has been ambiguous. On the basis of our current results and known literature data, we ascribe this band to the outermost hydration sphere of cations, which is possible to detect with IR spectroscopy, which depends on the kind of anion.

1. Introduction

The understanding of ionic hydration phenomena is a challenging problem for solution chemistry. Proper modeling of hydration processes seems necessary, as such processes are fundamental to chemical technology, biochemistry, and biology. Numerous experimental techniques, as well as theoretical simulations, have been applied to study the structure of water in electrolyte solutions. The plethora of available data has been summarized by many respected authors.[1−3]

Several conceptual models of ionic hydration have been proposed over the years. The one suggested by Frank and Wen[4] has been especially well acclaimed. Their picture of consecutive hydration spheres around a specific ion has proven to be essentially correct. Direct experimental methods, especially X-ray and neutron diffraction and X-ray absorption spectroscopy, have provided valuable insights into the structure of ionic hydration shells. Few reviews are available that summarize the experimental data along with computer simulation results.[5,6] Nevertheless, the interpretative and data treatment problems still preclude a full understanding of the influence of ions on water structure.

Multiple hydration spheres have frequently been detected by diffraction methods.[6] Despite the most "direct" character of these experiments, quantitative analysis of radial distribution functions at larger interatomic distances is difficult, and the final structural picture is less certain than for the first hydration sphere.

Vibrational spectroscopy is an ideally suited method for the investigation of solute hydration.[7,8] Spectra of isotopically diluted HDO in H_2O alleviate some of the experimental and interpretative problems connected with H_2O spectra.[9−11] Decoupled OD/OH water oscillators are a very sensitive probe of ionic hydration. To extract information about the water interactions inside the hydration sphere, the bulk water contribution has to be eliminated from the solution spectra, to obtain the solute-affected water spectrum. The relevant method of spectral data analysis was originally proposed by Lindgren and co-workers.[12] Quantitative versions of the method, along with a mathematical formalism, were formulated later.[13−15] A significant amount of data has been collected over the years, and a recent review summarizes the picture of ionic hydration emerging from it.[16] The most important conclusion is the "zone" model of cation hydration, resulting from the observation that cation-affected HDO band positions are not distributed in a continuous manner. Instead, they tend to group in fairly narrow (ca. 40 cm⁻¹ wide), distinct levels. The mean positions of these levels are 2200, 2420, 2533, and 2596 cm⁻¹.[16]

The level at 2200 ± 20 cm⁻¹ represents the highly structurized hydration shell of trivalent metal cations: Al^{3+}, Cr^{3+}, and Rh^{3+}. Apart from the primary affected HDO band at about 2200 cm⁻¹, another smaller band was detected at ca. 2420 cm⁻¹ and ascribed to the HDO molecules in the second hydration sphere.[17] An additional HDO band one energetic level up from the primary affected HDO band is a spectroscopic mark of the presence of second-shell interactions in the affected water spectrum.[16]

The level at 2420 ± 20 cm⁻¹ represents most divalent transition metal cations of the Mn^{2+}−Zn^{2+} series, as well as Mg^{2+}, Cd^{2+}, Hg^{2+}, and the lanthanides.[16] It also describes the water interactions around Li^+ ion in its first hydration sphere,[16] although some authors have not found the band of HDO affected by Li^+ in this region.[18]

The level at 2533 ± 20 cm⁻¹ describes the hydration of alkali metal cations, Ca^{2+}, Ba^{2+}, and hydrophobic cations (such as Ph_4P^+ or Bu_4N^+).[16] It also reveals the second hydration sphere of the Ni^{2+} cation: this band was first detected by Lindgren and co-workers and ascribed to the anion−water interactions of HDO with OD oscillators pointing away from the SO_4^{2-} anion.[19] It was later proposed that it is more probably attributable to the interactions in the cation's second hydration sphere, in

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parallel with the trivalent ions mentioned earlier.[16] The second HDO band of the hydrated lithium cation also lies at this level. It is still questionable to date, however, whether this band represents the second hydration sphere of this cation or the six-coordinated form of the cation, the four-coordinated counterpart of which belongs to the 2420 cm^{-1} level.[16]

The level at 2596 cm^{-1} was introduced on the basis of one instance only, namely, the NaF salt.[19] The original interpretation was similar to that presented earlier for the Ni^{2+} cation, with F$^-$ behaving similarly to SO$_4{}^{2-}$. Later, this band was ascribed to the HDO molecules in the second hydration sphere of Na$^+$, following the discussion for Ni^{2+}.[16]

In each of the discussed cases, the band position of HDO affected by the cation in its second hydration sphere lies one level up (in the direction of higher wavenumbers) from the respective position for the first hydration sphere, and so on for higher levels (cf. Figure 5 in ref 16). There is also at least a theoretical possibility that even further coordination spheres might be detected in this way, but this cannot yet be confirmed with the available experimental data.

As already mentioned, in the case of the Na$^+$ cation, the band ascribed formerly to the second-hydration-sphere HDO molecules lies at 2596 cm^{-1}.[16] We have observed or expected a similar small band situated at ca. 2600 cm^{-1} in many cases, but it was frequently overlapped by the anion-affected HDO band. To achieve maximum band separation, we decided to investigate the solutions of alkali metal hexafluorophosphates. The unique structural properties of the PF$_6{}^-$ anion in aqueous solution were observed for the first time in the pioneering Raman work of Walrafen. A split band of anion-affected HDO was detected at 2670 and 2660 cm^{-1}.[20] An IR result of 2665 cm^{-1} was also quoted by the author. This value was later confirmed in a more detailed study by Lindgren and co-workers.[13] An almost complete separation of cation- and anion-affected HDO bands enables the detection of the otherwise poorly resolved band at ca. 2600 cm^{-1} with high certainty. However, the PF$_6{}^-$ anion is known to hydrolyze in water,[21] and ionic association in aqueous KPF$_6$ was inferred on the basis of conductivity and isopiestic measurements,[22] which makes quantitative studies difficult. Nevertheless, in this work, we try to study lithium, sodium, and potassium hexafluorophosphates in aqueous solutions to discover the nature of the 2600 cm^{-1} affected HDO band. We also propose a reinterpretation of available experimental data on this band.

2. Experimental Section

2.1. FTIR Measurements. Potassium hexafluorophosphate (KPF$_6$, 99.9%), sodium hexafluorophosphate (NaPF$_6$, 98%), and lithium hexafluorophosphate (LiPF$_6$, 99.9%) were purchased from Aldrich and used without further purification. Analysis was performed for solutions of the following molalities: for KPF$_6$, 0.0973, 0.1934, 0.2449, 0.2908, and 0.3832 mol·kg^{-1}; for NaPF$_6$, 0.1941, 0.3892, 0.5796, 0.7750, and 0.9965 mol·kg^{-1}; and for LiPF$_6$, 0.0972, 0.1969, and 0.3003 mol·kg^{-1}.

Stock solutions were prepared by dissolving weighed amounts of the respective salts in redistilled water. The series of solutions were then prepared by dissolving weighed amounts of the respective stock solution in redistilled water. Sample solutions were made by adding 4% (by weight) of D$_2$O relative to H$_2$O and reference solutions by adding the same molar amounts of H$_2$O. Densities of solutions were measured by weighing pipetted volumes at 25.0 ± 0.5 °C.

FTIR spectra were recorded on an IFS 66 Bruker spectrometer. Two hundred fifty-six scans were made with a selected
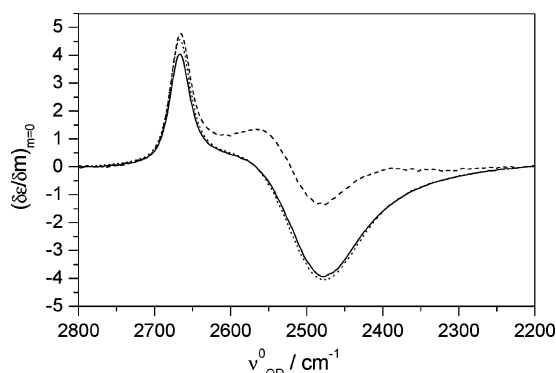
Figure 1. Derivatives $(\partial \epsilon / \partial m)_{m=0}$ for aqueous solutions of LiPF$_6$ (- - -), NaPF$_6$ (—), and KPF$_6$ (•••) for linear relationship of ϵ vs m.

resolution of 4 cm^{-1}. A cell with CaF$_2$ windows was employed. The path length was 0.0298 mm, as determined interferometrically. The temperature was kept at 25.0 ± 0.1 °C by circulating thermostated water through mounting plates of the cell. The temperature was monitored by a thermocouple inside the cell.

The spectra were analyzed by commercial programs GRAMS/ 32 4.01 (Galactic Industries Corporation, Salem, MA) and RAZOR (Spectrum Square Associates, Inc., Ithaca, NY) run under GRAMS/32.

2.2. Analysis of Spectral Data. Spectral data were analyzed such that the contribution of the bulk water was removed from the solution spectra to separate the spectra of solute-affected water only. The procedure, known as the difference spectra method, has been described in ref 15. It is based on the assumption that water in solution can be divided into additive contributions of bulk (b) and solute-affected (a) water. The vibrational spectrum of the latter, ϵ_a, can be calculated for each wavenumber from eq 1

$$\epsilon_a = \frac{1}{NM}\left(\frac{\partial \epsilon}{\partial m}\right)_{m=0} + \epsilon_b \qquad (1)$$

whereas the spectrum of the former is, by definition, identical to the pure HDO spectrum, ϵ_b; M denotes mean molecular weight of solvent (H$_2$O + 4% D$_2$O) (kg·mol^{-1}).

An approximation of the experimental spectrum $\epsilon(\nu_i)$ vs molality m at each wavenumber ν_i by the least-squares method allows extrapolation of the spectrum of solute-affected water to infinite-dilution conditions, assuming that the "affected number", N, is known. This parameter is equal to the number of moles of water affected by one mole of solute. A proper value for N can be found using the published algorithm.[15]

The procedure of finding the solute-affected water spectrum consists of computer simulation of the difference spectra using the baseline, analytical bands and the bulk water spectrum. The spectra presented herein could be well resolved into four component bands. The product of Gaussian and Lorentzian peak functions was found as the best function for fitting the experimental difference spectra.

3. Results and Discussion

In Figure 1, derivatives $(d\epsilon/dm)_{m=0}$ vs wavenumber are shown for a linear approximation of ϵ vs m, which was found to be the most justified approximation on the basis of the obtained spectral data (judging by the value of determination coefficient, $R^2 \geq 0.9999$). The linear relationship means that the salt-affected water spectrum does not change with molality, which reflects additivity for cation- and anion-affected water.
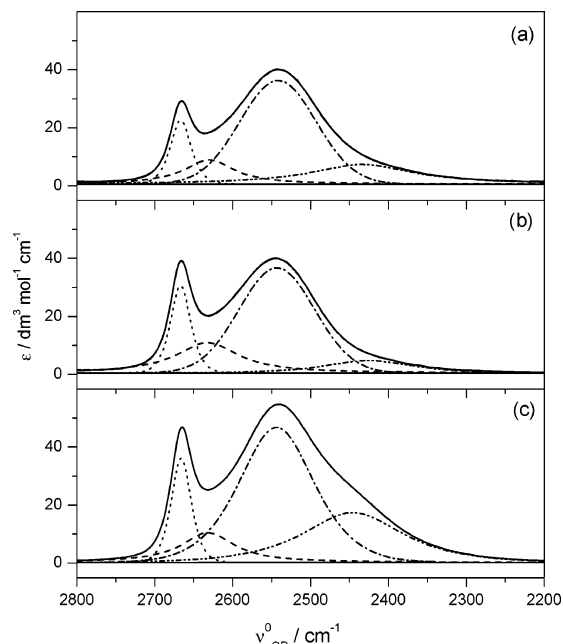
Figure 2. Decomposition of the final difference spectra of HDO affected by (a) KPF$_6$, (b) NaPF$_6$, and (c) LiPF$_6$ into component bands.

**TABLE 1: Parameters of Component Bands from the Decomposition of the HDO Spectra Affected by KPF$_6$, NaPF$_6$, and LiPF$_6$**

KPF$_6$			NaPF$_6$			LiPF$_6$		
ν_{OD}^0 [a]	fwhh[b]	shape[c]	ν_{OD}^0 [a]	fwhh[b]	shape[c]	ν_{OD}^0 [a]	fwhh[b]	shape[c]
2667	32	G × L	2667	32	G × L	2666	34	G × L
2630	79	L	2632	98	L	2631	82	L
2541	115	G	2543	114	G	2543	117	G × L
2433	150	L	2425	133	G × L	2445	150	G × L

[a] Band position at maximum (cm^{-1}). [b] Full width at half-height (cm^{-1}). [c] G, Gaussian band; L, Lorentzian band.

The difference spectrum for the maximum value of N, which does not contain any contribution of the bulk HDO spectrum, is regarded as the affected spectrum. After the adjusting procedure, the affected numbers N were found to be equal to 9.8 for KPF$_6$, 7.7 for NaPF$_6$, and 6.6 for LiPF$_6$. In all three cases, the contribution of the bulk water spectrum did not exceed 0.5% of the total integrated intensity. Figure 2 summarizes the band shape analysis, showing the salt-affected spectra at infinite dilution for the adjusted N values. The respective component band positions are listed in Table 1. The shapes of the solute-affected water spectra are additionally compared in Figure 3, along with the bulk water spectrum.

Two low-wavenumber components for each studied salt can be definitely ascribed to HDO affected by the respective cation. In the case of the K$^+$ and Na$^+$ cations, a small component band at ca. 2430 cm^{-1} can be noticed in the affected water spectra, but we treat this rather as an asymmetry correction of the main cation-affected band, rather than a separate component, as is the case for Li$^+$. The affected HDO bands for Na$^+$ and K$^+$ might as well be approximately described by a single asymmetric log-normal curve. Although such an approach has been previously used in the works from our laboratory,[14] the fit is much better with the "tail" component added explicitly. For Li$^+$, it is impossible to reach a satisfactory fit with one asymmetric component only, and thus both components have physical significance.

A band situated at ca. 2667 cm^{-1} is clearly visible in the spectra of affected water for all studied solutes. This band has
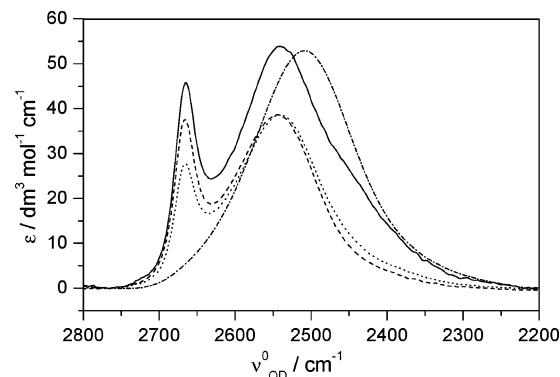
Figure 3. Comparison of difference spectra of LiPF$_6$ (—), NaPF$_6$ (- - -), and KPF$_6$ (•••) for final adjusted N values. The spectrum of bulk HDO (- • - • -) is also shown.

been described earlier.[13,20] It corresponds to HDO molecules affected by the PF$_6^-$ anion, which is a strong structure breaker and exhibits extremely weak interactions with water. The ν_{OD}^0 value in this case (2666 cm^{-1}) is clearly higher than ν_{OD}^0 for HDO molecules, which do not form any hydrogen bonds with H$_2$O in a water environment (2644 cm^{-1}, see ref 16 and ref 38 cited therein). It is well-known[23] that the HDO band position generally depends on both H-bond formation and van der Waals interactions. In the discussed case, the H-bond strength should depend on two effects: ion−dipole interactions and electron delocalization (covalent component of the H-bond). The second effect decreases rapidly with decreasing ion−dipole interaction. The ion−dipole interaction of water molecules with PF$_6^-$ ions seems to be very weak, as it has only a minor influence on the OD band position. A certain measure of such an effect could be provided by the band position of monomeric HDO screened from interacting with other species by the CF$_3$ ends of aggregated CF$_3$COO$^-$ or CF$_3$SO$_3^-$ anions (ca. 2690 cm^{-1}), as previously established[24,25] and further confirmed.[16] The band shift from 2690 to 2667 cm^{-1}, when ascribed to the ion−dipole interaction, seems to be an overestimation of this effect however, because of possible H-bond formation by HDO interacting with PF$_6^-$ with the bulk phase via lone electron pairs. From the arguments cited above, it appears that the blue shift of the band of HDO affected by the PF$_6^-$ ion relative to that of non-H-bonded water can be explained by weaker London dispersive forces (usually the main contribution to the van der Waals forces) between water and the fluorine atoms of PF$_6^-$ rather than those between water molecules.

The variation of the N value with cation can be justified by the consistency of the PF$_6^-$-affected HDO band, when scaled to an absorbance scale. The value of N is directly proportional to the affected HDO concentration (see ref 14). Isolated anion-affected component bands (expressed as molar absorption coefficients), when multiplied by N, are thus proportional to the HDO absorbance in the anion hydration sphere. This should be additionally scaled, assuming a means of dividing the N value into cation- and anion-dependent parts. Because there is a common anion in all salts, the latter procedure can be neglected. As seen in Figure 4, the integrated intensity of this band on an absorbance scale is almost constant, indicating a coherent set of N values for the studied solutions.

The affected number (N) reflects the number of water molecules that can be spectroscopically distinguished from the bulk phase. The N values are often small when compared with the actual number of water molecules in the vicinity of a solute.[15] However, when the state of water molecules differs strongly (as manifested by a large band shift or a very narrow band)

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TABLE 2: Position of Maximum of OD Band of HDO Affected by Anions and HDO Affected by Cation and Anion

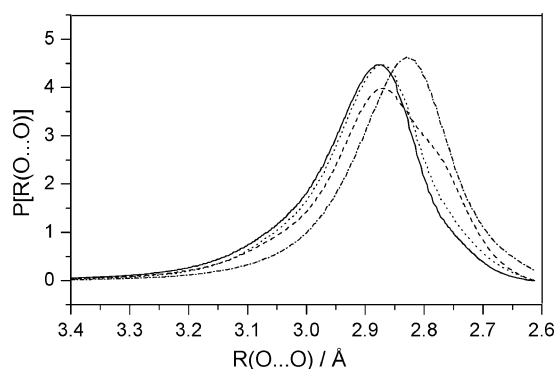| no.[a]	anion	ν^0_{OD} (anion)[b]	ref	cation[c]	ν^0_{OD} (cation + anion)[d]	ref
1	PO$_4^{3-}$	2294	35	K$^+$ (2°)	2597	35
2	OH$^-$	2437	36	Li$^+$ (2°/3°)	2608	36
3	OH$^-$	2448	36	Na$^+$ (2°)	2614	36
4	HPO$_4^{2-}$	2433	35	K$^+$ (2°)	2609	35
5	F$^-$	2472	18	Na$^+$ (2°)	2596	18
6	F$^-$	2445	26	Na$^+$ (2°)	2620	26
7	H$_2$PO$_4^-$	2601	35	K$^+$ (2°)	2601	35
8	H$_2$PO$_4^-$	2601	35	H$^+$ (?)	2621	35
9	ClO$_4^-$	2630	12−14,18, 26−29,31, 34, 37−39	Mg^{2+} (3°) Ni^{2+} (3°)	2620 2620	34 34
10	PF$_6^-$	2667	13, this work	K$^+$ (2°) Na$^+$ (2°) Li$^+$ (2°/3°)	2630 2632 2631	this work this work this work
11	PF$_6^-$	2667	13, this work	H$^+$ (?)	2613	36

[a] Numbers refer to data points in Figure 6. [b] Band position of anion-affected water at maximum (cm^{-1}). [c] Proposed hydration sphere number shown in parentheses (2°, second hydration sphere; 3°, third hydration sphere; ?, see explanation in text). [d] Band position of (cation + anion)-affected water at maximum (cm^{-1}).
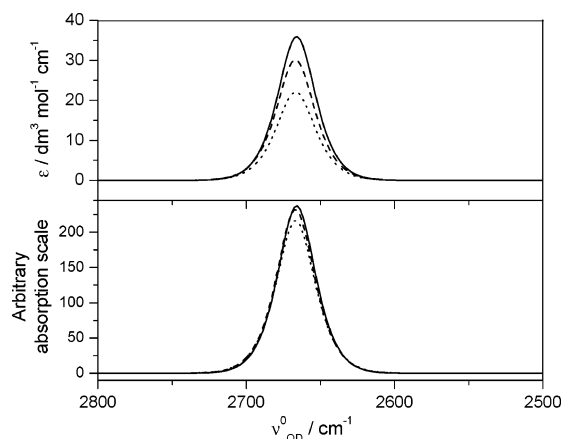
Figure 4. Comparison of anion-affected HDO bands from the difference spectra of LiPF$_6$ (—), NaPF$_6$ (- - -) and KPF$_6$ (⋯): (top) molar absorption coefficient scale and (bottom) rescaled by adjusted N values.

Figure 5. Interatomic O⋯O distance distributions derived from the spectra of HDO affected by K$^+$ (—), Na$^+$ (⋯), and Li$^+$ (- - -) along with bulk HDO distance distribution curve (- · - · -).

from the bulk phase then N often corresponds to the hydration numbers obtained from diffraction methods.[26,27] Computer simulations and diffraction experiments predict hydration numbers of 6−8 for K$^+$, 6 for Na$^+$, and 6 or 4 for Li$^+$.[5,6] In a previous work,[28] we obtained $N = 7$ for NaClO$_4$, and it is also known that ClO$_4^-$ affects ca. 2 HDO molecules.[13,19,29] In this work, we obtained $N = 7.7$ for NaPF$_6$; hence, the PF$_6^-$ anion affects ca. 3 HDO molecules. Consequently, we have obtained N equal to almost 7 for K$^+$, almost 6 for Na$^+$, and almost 4 for Li$^+$. It should be noticed that the position of the cation-affected HDO band at ca. 2540 cm^{-1} differs only slightly from the bulk HDO band position at 2509 cm^{-1}. The Li$^+$-affected HDO band consists of two components having physical significance: the component at 2445 cm^{-1} corresponds to the hydration of four-coordinated Li$^+$, and the intense component at 2543 cm^{-1} corresponds to the hydration of six-coordinated Li$^+$ or to the second hydration sphere of the four-coordinated cation, as previously anticipated.[16] The low value of N obtained in this work for LiPF$_6$ suggests rather an equilibrium between four- and six-coordinated lithium cation. For another case, namely, four water molecules in the first hydration sphere (2445 cm^{-1} band) and a well-defined second sphere (2543 cm^{-1} band), we would have expected a higher N value than presently obtained.

Examination of the interatomic O⋯O distance distribution curves, which can be directly obtained from the HDO band

shapes, further strengthens the interpretation of cation-affected HDO band. A number of correlations linking $R_{O\cdots O}$ and ν_{OD} have been published, based mainly on crystalline hydrates data.[30] The probability distribution P as a function of $R_{O\cdots O}$ can then be calculated from the absorption curve.[31] The numerical procedure and necessary assumptions to the method have been previously discussed.[15] The interatomic O⋯O distance distribution curves obtained from the affected water spectra from Figure 3 are shown in Figure 5. Prior to calculation of the $P(R)$ curve, the anion-affected HDO band was subtracted from the difference spectra, to reflect solely the cationic effect on the HDO distance distribution. The curve for the Li$^+$ cation obviously contains a component at lower distance (ca. 2.75 Å), apparently absent for the two other cations.

Apart from the previously observed and described bands, a new component band at ca. 2630 cm^{-1} is present in the affected water spectra of the studied solutes. This band has been detected for many inorganic salts, and its interpretation thus far has been ambiguous. It is usually weak and frequently not visible because of superposition with the anion-affected, cation-affected, or bulk water bands. In the case of solutions for which it is observed, its position varies within the 2596−2632 cm^{-1} region. In ref 16, the discussed band (at ca. 2600 cm^{-1}) was ascribed to interactions of water in the second hydration sphere of the Na$^+$ cation or to water molecules in the first hydration sphere that interact more weakly with the cation. On the basis of the current results, we ascribe this band to the water molecules in the outer hydration spheres of the studied cations that depend on the kind
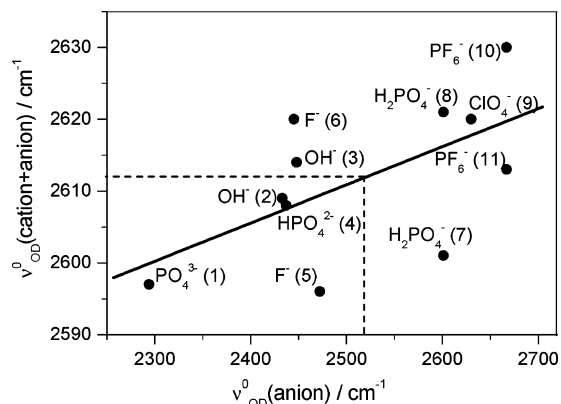
Figure 6. Dependence of ν_{OD}^0(cation + anion) on ν_{OD}^0(anion) from experimental data and the predicted linear relationship (—). The numerical point labels refer to respective entries in Table 2. Dashed lines illustrate the point for ν_{OD}^0(anion) = ν_{OD}^0(bulk) (see explanations in text).

of anion; the respective data are included in Table 2. Generally, the discussed band might correspond to the furthest detectable hydration sphere of the cation, the exact location of which follows from its position in the zone cation hydration model[16] (see Table 2). In most cases, the order of this hydration sphere can be unambiguously determined. Two cations apparently require further elucidation, namely, Li$^+$ and H$^+$. For lithium, on the basis of the rather low N value obtained here for LiPF$_6$, the spectra most probably reflect the tetrahedral/octahedral isomerism of the hydrated cation complex in its first hydration sphere. Consequently, the high-wavenumber component should be ascribed to the third hydration sphere of the tetrahedral complex (primary band at 2445 cm^{-1}) or to the second sphere of the octahedral complex (primary band at 2543 cm^{-1}). The hydrated proton complex, in turn, has many exceptional properties, so we prefer to refrain from any final judgment as to the origin of the high-wavenumber component. Results from future theoretical studies might help in assignment of the H$^+$-affected HDO band.

Although our methodology assumes extrapolation to infinite-dilution conditions, the molality of the studied solutions (on the order of 0.1−1 mol kg^{-1}) is, nevertheless, at least 2 orders of magnitude higher than what is supposed to be a "dilute" aqueous solution. Therefore, the possibility of outer-sphere ion association cannot be arbitrarily excluded, and its influence on the difference spectra might manifest itself through common cation- + anion-affected HDO bands. A similar interpretation was presented as early as 1970 by Kęcki et al.,[32,33] although their "trapped" HDO molecules (shared by anion and cation hydration spheres), with a band position 2634 cm^{-1}, are now known to be affected solely by the perchlorate anion. A more up-to-date approach was proposed by Kristiansson and Lindgren.[34] The band positions of HDO affected supposedly by solvent-shared ion pairs reported by them agree well with our current results (cf. Table 2). The only difference lies in the interpretation of results: instead of considering a direct outer-sphere association, we rather opt for a more remote cation−anion contact, with the anion exerting its effect on the water molecules in the outer hydration spheres of cation. This effect is almost cation-independent, and the discussed band's position, ν_{OD}^0(cation + anion), correlates adequately with the band position of anion-affected water, ν_{OD}^0(anion). The positions of the ν_{OD}^0(anion) vs ν_{OD}^0(cation + anion) component bands for affected HDO in different solutions are summarized in Table 2. The predicted correlation between these data is presented in Figure 6.

Using this correlation, we are able to predict the ν_{OD}^0(cation + anion) band position for the hypothetical situation in which there is no anionic effect on bulk water (the anion-affected HDO band is identical to the bulk water band). The procedure is very similar to the one applied earlier in the study of tetrabutylammonium cation hydration.[15] The intersection of the 2509 cm^{-1} abscissa (the position of the bulk HDO band maximum) with the correlation line gives an ordinate of ca. 2611 cm^{-1}, which can be considered as the position of the ν_{OD}^0(cation + anion) band in the absence of an anion. The expected error, predicted from the scatter of experimental values, is about 20 cm^{-1}. The hypothetical position of this band, rescaled to interatomic distance as described above, gives an $R_{O\cdots O}$ value 3.02 Å, clearly indicating the existence of a structure-breaking effect of the cation in its further hydration spheres. This, in turn, suggests that the model of Frank and Wen,[4] with a disordered region encircling the cation's hydration shell, is essentially correct.

4. Conclusions

Infrared difference spectra provided us with additional valuable information on cation hydration spheres in aqueous solutions. Careful selection of an anion for this study allowed us to separate the effects of cations and anions to the maximum possible extent. In the presence of the PF$_6^-$ anion, the high-wavenumber part of the cation-affected band is accessible to component analysis with precision unattainable elsewhere. We have ascribed this component band to the water molecules in the outermost detectable hydration sphere of the cation, depending on the kind of anion. Its relatively high frequency supports the view that cations exert a structure-breaking effect outside their hydration shell. This effect is cooperative, as the position of this band depends approximately linearly on the position of anion-affected HDO band.

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