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IR Study of Cation Effects on the O—D Stretching Frequencies of Isotopically Dilute HDO in Aqueous Salt Solutions*

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IR spectra of 3 normal solutions of 14 different salts [chlorides of Al^{+++}, Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Zn^{++}, Cd^{++}, Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, $N(CH_3)_4{}^{+}$] in both, 96% H_2O + 4% D_2O and 100% H_2O, were measured in the frequency range $\bar{\nu} = 2\,800$–$2\,100\,cm^{-1}$. From up to 18 single measurements for each solution the frequencies and halfwidths of the O—D stretching bands of isotopically dilute HDO were determined with high accuracy. Frequencies in the range $\bar{\nu} = 2\,510$–$2\,529\,cm^{-1}$ and halfwidths in the range $\Delta\bar{\nu}_{1/2} = 155$–$205\,cm^{-1}$ resulted at $T = 30\,°C$ with standard deviations typical less than $\pm 1\,cm^{-1}$ and $\pm 4\,cm^{-1}$, respectively. An almost perfect correlation between the O—D stretching band parameters and the polarizing power of the cations was obtained.

(Keywords: IR spectra; HDO *Stretching frequencies; Salt solutions; Cation effects)*

IR Untersuchung von Kationeneffekten auf die O—D *Streckfrequenzen von isotopenverdünntem* HDO *in wäßrigen Salz-Lösungen*

Es wurden IR-Spektren von 3 normalen Lösungen 14 verschiedener Salze [Chloride von Al^{+++}, Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Zn^{++}, Cd^{++}, Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, $N(CH_3)_4{}^{+}$] in 96% H_2O + 4% D_2O und in 100% H_2O gemessen (Frequenzbereich $\bar{\nu} = 2\,800$—$2\,100\,cm^{-1}$). Aus bis zu 18 Einzelmessungen für jede Lösung wurden die Frequenzen und Halbwertsbreiten der O—D-Valenzbanden von isotopenverdünntem HDO mit hoher Genauigkeit bestimmt. Bei $T = 30\,°C$ wurden Frequenzen im Bereich $\bar{\nu} = 2\,510$—$2\,529\,cm^{-1}$ und Halbwertsbreiten im Bereich $\Delta\bar{\nu}_{1/2} = 155$—$205\,cm^{-1}$ erhalten, wobei die Standardabweichungen typisch kleiner als $\pm 1\,cm^{-1}$, bzw. $\pm 4\,cm^{-1}$ waren. Es wurde eine nahezu perfekte Korrelation zwischen den Parametern der O—D-Valenzbanden einerseits, und dem Ladungs-Radius-Verhältnis der Kationen andererseits gefunden.

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Introduction

The stretching frequency region of the vibrational spectrum of water in aqueous salt solutions has already been subjected to extensive investigations and experimental data are available for a large number of salts[1,2]. In particular, since the vibrational spectrum of HDO is much more simpler than that of H_2O or of D_2O, the isotopic dilution technique (dilute HDO in H_2O or in D_2O) has become a well established method. The IR spectrum of dilute HDO in H_2O exhibits one roughly *Gauss*ian shaped O—D stretching band with a band maximum at 2 510 cm^{-1} and a halfwidth of 165 cm^{-1} at room temperature[3]. Apart from some exceptional cases, such as perchlorates or tetrafluoroborates[4], the IR spectra of HDO in most salt solutions closely resemble that of HDO in pure H_2O, with the frequencies of the band maximum slightly shifted and the halfwidths somewhat changed. These changes are representative of the effects produced by both, cations and anions, and the frequency shifts may be taken as a measure of some kind of average hydrogen bond strength in the solutions[2].

Basically, the cation-water interaction, which causes a dielectric polarization of the water molecules, should increase with increasing cation charge and decreasing ionic radius, as already proposed by *Bernal* and *Fowler*[5], and, hence, the water stretching frequencies should decrease with increasing cation surface charge density. This relationship is generally accepted and has for instance been confirmed by various model calculations on cation-water pairs[6,7], from which shifts of several hundred wavenumbers resulted. From an experimental point of view the cation effects should be accessible from IR or *Raman* measurements of solutions containing a common anion. Of course, the actual values of the single cation effects can not be directly obtained in this way, since the observed spectra result from the total water of the solution, which, to a first approximation, consists of three subsystems: bulk water, anion hydration water and cation hydration water. However, to a first approximation the contributions of the first two subsystems may be assumed to be constant for solutions with unique anion concentration and the differences observed for solutions with different cations should yield at least the correct trends of the cation effects. Unfortunately, an inspection of the spectroscopic data available in the literature does not provide very satisfactory results. On the one hand, frequency shifts only within the spectral resolution, as well as shifts of more than hundred wavenumbers have been reported by different authors in the elder literature[8—10], while on the other hand, the number of more recent high quality data is rather small.

In the present paper frequencies and halfwidths of the O—D stretching bands of dilute HDO are reported for solutions of 14 different salts with chloride as a common anion and with unique, 3 normal, salt concentration. Special attention was paid to an utmost accurate determination of the band parameters at unique temperature. The data shall provide reliable quantitative information about the effects of a larger number of different cations on the water stretching bands in aqueous salt solutions.

Experimental

IR spectra of 3 normal solutions, $pH = 4$, of $N(CH_3)_4Cl$ and of 13 metal chlorides (see Table 1) in both, 96% H_2O + 4% D_2O and 100% H_2O, were measured in the frequency range $\bar{\nu} = 2\,800$–$2\,100\,cm^{-1}$. A CaF_2 cell with a pathlength of $d = 0.025$ mm was used, except for the solutions of $BeCl_2$ and $AlCl_3$. The latter were found to affect the CaF_2 windows and, therefore, AgCl throwaway cells with $d = 0.025$ mm were used. The spectra were measured without reference cell with a Perkin-Elmer 580 B spectrometer, which was on line connected to a PE 3 500 data station. The spectral resolution was about $2\,cm^{-1}$ (integrated scan mode 6 B).

In order to obtain the parameters of the O—D stretching bands of HDO, the spectra were processed in the following way, making use of the standard routines of the PE 580 applications program: 1. The spectra of an isotopically dilute salt solution, denoted S ("sample"), and of a corresponding 100% H_2O salt solution, denoted R ("reference"), both measured at the same temperature within ± 0.5 °C, were converted from transmittance to absorbance units. 2. To account for the inherent differences between 100% H_2O and 96% H_2O + 4% D_2O solutions and for possible small variations of the cell pathlength, spectrum R was corrected by a small factor, which was numerically evaluated by equalizing the absorbance of R at $2\,100\,cm^{-1}$ to that of S at $2\,100\,cm^{-1}$. 3. A difference spectrum, $D = S—R_{corr}$, was computed (see Fig. 1 for typical spectra), which, besides an almost neglegible contribution from D_2O, essentially consists of the O—D stretching band of HDO only. 4. The halfwidth of the O—D stretching band was graphically determined from D. 5. The frequency of the O—D stretching band was numerically determined from D.

From extensive test measurements with pure 96% H_2O + 4% D_2O (sample) and 100% H_2O (reference) it became apparent, that the values obtained by single frequency determinations as described above may vary by as much as $\pm 3\,cm^{-1}$. Moreover, the frequency of the O—D stretching band of HDO is known to increase by about $0.5\,cm^{-1}\,deg^{-1}$ with increasing temperature[3]. In order to improve the accuracy of the frequency determination and to account for the temperature dependence 12–18 spectra of each sample solution and each reference solution were recorded in the temperature range $T = 25$–36 °C, with the exception of $BeCl_2$ and $AlCl_3$, where only 6 single spectra were recorded for each solution. The temperatures were monitored during the measurements and varied by less than one degree. With the single frequency values, $\bar{\nu}(T)$, a linear regression of the type $\bar{\nu}(T) = \bar{\nu}_0 + k \cdot T$ was performed for each salt solution and k-values of 0.25–$0.50\,cm^{-1}\,deg^{-1}$ and standard deviations of less than $\pm 1\,cm^{-1}$ ($\pm 2.5\,cm^{-1}$ for $BeCl_2$ and $AlCl_3$) resulted. As final results the frequency values from the regression lines at $T = 30$ °C were chosen. As to the halfwidths of the O—D stretching bands, the temperature dependences were not significant within the experimental

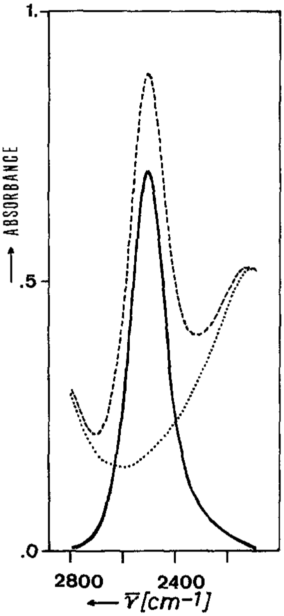

Fig. 1. IR spectra of 3 *N* KCl solutions: a) 96% H_2O + 4% D_2O (dashed line); b) 100% H_2O (dotted line); c) difference spectrum, a–b (full line)

accuracy. Simply mean values of the single half width values were, therefore, taken as final results, the rms deviations of which were less than $\pm 4\,\mathrm{cm}^{-1}$ ($\pm 7\,\mathrm{cm}^{-1}$ for $BeCl_2$ and $AlCl_3$).

Results and Discussion

The results are summarized in Table 1, which also contains data about some properties of the cations. Additionally, Fig. 2 shows a plot of the O—D stretching band parameters versus the polarizing power of the cations*, which has widely been used in similar correlations[13] instead of the simple charge/radius ratio. As to the ionic radii given in Table 1, it should be noted, that they are shomewhat arbitrary, not only with respect to the method of determination, but also and particularly with respect to the coordination number considered. The data of Table 1 refer to coordination number VI, although coordination number IV would possibly be more appropriate in one or the other case, for instance for Cd^{++} [14]. The differences are, however, not large enough to significantly affect the correlations of Fig. 2 and the results drawn from it.

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* Polarizing power: $P = z/(r \cdot S_{\mathrm{eff}})$; z (charge), r (atomic radius), S_{eff} (screening factor)[12].

Table 1. *Frequencies and halfwidths of* O—D *stretching bands of dilute* HDO *in* 3 *N salt solutions (pH = 4; T = 30 °C; for accuracy see text); ionic radii for coordination number VI, r (Ref.*[11]*) and polarizing powers, P (Ref.*[12]*) of cations*

	$\bar{\nu}$ [cm^{-1}]	$\Delta\bar{\nu}^{a}$ [cm^{-1}]	$\Delta\bar{\nu}_{1/2}$ [cm^{-1}]	r [Å]	P
pure H_2O	2514.5	0.0	165		
$N(CH_3)_4Cl$	2529.0	—14.5	160		(0.3)[b]
CsCl	2527.0	—12.5	155	1.70	0.60
RbCl	2528.0	—13.5	155	1.49	0.68
KCl	2528.0	—13.5	155	1.38	0.74
NaCl	2527.0	—12.5	155	1.02	1.02
LiCl	2520.0	—5.5	165	0.74	1.26
$BaCl_2$	2523.5	—9.0	160	1.36	1.42
$SrCl_2$	2522.0	—7.5	160	1.16	1.69
$CaCl_2$	2520.0	—5.5	165	1.00	1.97
$MgCl_2$	2514.5	0.0	175	0.72	2.93
$BeCl_2$	2512.0	2.5	185	0.35	5.10
$CdCl_2$	2516.5	—2.0	165	0.95	2.88
$ZnCl_2$	2514.0	0.5	180	0.75	3.46
$AlCl_3$	2510.0	4.5	205	0.53	5.82

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[a] $\Delta\bar{\nu} = \bar{\nu}(H_2O) - \bar{\nu}$.

[b] $1/r$, estimated from crystallographic data.

From Table 1 and Fig. 2 it can be seen that the differences between the O—D stretching band parameters of the different salt solutions are rather small, for instance the frequencies cover a total range of less than 20 cm^{-1} only. Nevertheless the expected correlation, i.e. decreasing frequencies with increasing cation charge and decreasing ionic radius and a corresponding increase of the halfwidths, is obvious. For a more precise and quantitative comparison only the data of equally charged cations should be considered, because the chloride concentration was the same for all solutions and, therefore, the concentration of monovalent cations was twice that of divalent ones and three times that of Al^{+++}. As to the monovalent cations, with the exception of Li^{+}, the observed band parameters are about equal within the experimental accuracy, including those of $N(CH_3)_4{}^{+}$, which is by far the largest cation of the whole series. These values apparently establish the limits for 3 normal chloride solutions containing cations with small surface charge density. As expected, the other extreme values—lowest frequency and largest halfwidth—are obtained for Al^{+++}, which has the highest polarizing power among the cations included in this study. The band parameters of

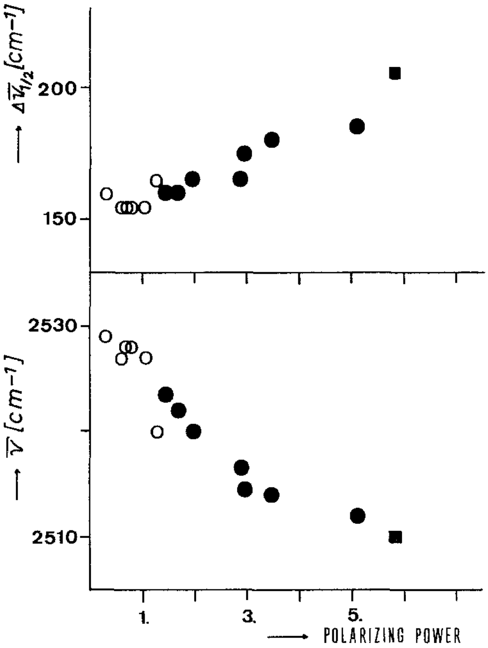

Fig. 2. O—D stretching band parameters of dilute HDO in 3 *N* chloride solutions versus polarizing power of the cations: ○ monovalent cations; ● divalent cations; ■ trivalent cations

the divalent cations are found just between these limits and, moreover, the correlation between the band parameters and the polarizing power is almost perfect (Fig. 2). These findings are in good agreement with the results of cation effects in salt solutions obtained by other methods than the measurement of water fundamentals, such as near infrared spectroscopy[2] or nuclear magnetic resonance spectroscopy[15, 16].

As already noted in the introduction, only the correct trends, but not the actual values of the single cation effects can be directly deduced from the O—D stretching band parameters. It may, however, be noticeable, that very recently attempts have been made to obtain information about the actual contributions of the different water subsystems from both, experimental data and model calculations. In an IR study[17, 18] the contribution from the bulk water has been removed by calculating appropriate difference spectra and the remaining absorption was split into cation and anion hydration subbands by band-shape analyses. Promising and reasonable results have been obtained in this way mainly for salt solutions, which obviously exhibit large differences between cation and anion effects, as is for instance the case for perchlorates of divalent cations. However, the more the cation and anion hydration bands approach each other, the more problems arise and the technique could not be successfully applied, e.g. to a NaCl solution. Nevertheless, the data reported for the hydration bands of different cations also confirm the relationship between water stretching frequency and cation surface charge density. As to model calculations, molecular dynamics simulations of salt solutions[19] have been used to calculate the stretching band parameters of the three water subsystems. The frequency maxima for the total water obtained in this way are in excellent agreement with the data reported in the present paper, while for the cation hydration bands significantly lower frequency maxima resulted than those obtained in the IR study just mentioned.

On summarizing, from the data reported in the present paper it is evident, that, although the differences between the band parameters are rather small, the frequency maxima of the water stretching bands in salt solutions systematically depend on the cation surface charge density. The correlation obtained is highly satisfying. It is in full agreement with the predictions of the classical theory of electrolytes[5] and, as far as available, in agreement with the results of several other investigations about cation effects in salt solutions.

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