

Hydration of Ions in Aqueous Solutions Studied by Infrared Spectroscopy. I. Method

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A method has been developed for the study of hydration of ions in aqueous solutions by infrared spectroscopy. Spectra of isotopically diluted HDO molecules are recorded in the presence and absence of ions. Difference spectra are calculated to remove the contribution from the bulk water. A band-shape analysis is subsequently performed on the difference spectrum in which gaussian bands are used to simulate the observed bands.

Information on the hydration structure of ions in aqueous solutions from infrared studies has been rather limited due to the strong absorption of the bulk water. In a series of studies by Falk and co-workers^{1,2,3} and others (for a review see Ref. 4), an isotope dilution technique has been used in which the strong absorption from pure water is avoided. Moreover, the internal and external couplings of water molecules are removed, leading to narrower bands and simplifications in the interpretation of the spectra. Studies were made both in the OH- and OD-stretching regions. In studies of different perchlorate solutions,² relatively narrow bands at 3572 cm⁻¹ for OH and 2629 cm⁻¹ for OD vibrations were found to be associated with HDO molecules weakly hydrogen-bonded to the ClO₄⁻ ions. A second observed band was suggested to correspond to the remaining OH and OD groups in the solutions. No bands which could be associated with the hydration of the cations were resolved.

With the advent of low-noise computerized spectrometers however, it seemed worthwhile to find out whether it was possible to study the important though difficult problem of ion hydration, and actually to observe bands from cation hydration.

In this paper, we describe a method based on the isotope dilution technique. Spectra are recorded in the OD-stretching region 2900–1800 cm⁻¹. Difference spectra are calculated to observe the bands from hydrated ions, and a band-shape analysis is subsequently performed. In the following, we will use the example of a Fe(ClO₄)₂ solution to demonstrate the procedure.

EXPERIMENTAL

Analytic grade Fe(ClO₄)₂·6H₂O was used for the preparation of the solutions. An Fe²⁺ ion concentration of 0.4 molal was used. Spectra for four solutions were recorded: for pure H₂O, H₂O containing 1 % D₂O, for the salt solution and for the salt solution containing 1 % D₂O. The temperature of a cell equipped with CaF₂ windows and a teflon spacer was regulated by circulating water through the mounting plates of the cell. The temperature used in the experiments was 20.0(1) °C, as measured by a thermocouple inserted in the solution in the cell. The path length was 0.0270(2) mm (determined interferometrically). The cell was remounted and cleaned between each measurement.

A Perkin-Elmer 580B spectrometer on-line with the Perkin-Elmer Data Station 3500 was used for the registration of the spectra. The resolution selected was ~10 cm⁻¹, in order to minimize the noise. About 16 scans were made in about 60 min in the region 2900–1800 cm⁻¹; the average was taken. This scan procedure was found to be preferable to one using the same time for a single scan, since CO₂(g) bands were averaged more satisfactorily.

Band-shape analysis. The evaluation of the spectra was performed in two steps. The first is

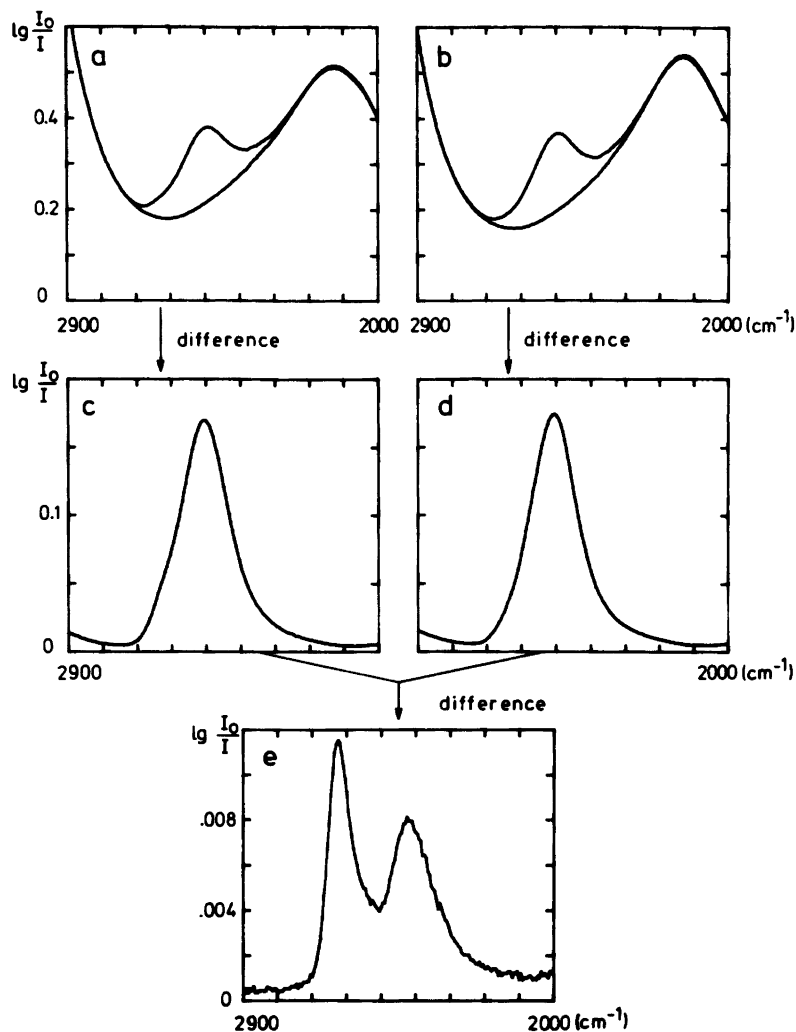


Fig. 1. IR absorption spectra of aqueous solutions at 20.0 °C with a cell thickness of 0.0270 mm and CaF₂ windows. (a) Spectra of 0.400 molal Fe(ClO₄)₂ containing 2 % HDO (upper spectrum) and 0.400 molal Fe(ClO₄)₂ (lower spectrum). (b) Spectra of water containing 2 % HDO (upper spectrum) and pure water (lower spectrum). (c) Difference spectrum derived from spectra in (a). (d) Difference spectrum derived from spectra in (b). (e) Difference spectrum derived from (c) and (d).

illustrated in Figs. 1a and c, where a difference was calculated between spectra of the Fe(ClO₄)₂ solution containing 2 % HDO and the pure Fe(ClO₄)₂ solution. Similarly, a difference was calculated between spectra of water containing 2 % HDO and pure water (Figs. 1b and d). The spectra of the solutions containing no deuterium were multiplied by 0.98 before the differences were made. This procedure using two separate differences was necessary since the more direct

method of using a difference between the upper spectra in Figs. 1a and b gave poor results. One reason for this is the terminating absorption from the OH stretching band found in the high wavenumber part of the spectra. In Fig. 1a this OH absorption is displaced towards lower wavenumbers relative to the corresponding part in Fig. 1b. This displacement is caused by the absorption from hydrated Fe²⁺ ions. Furthermore, the combination band at ~2120 cm⁻¹ has a

different band-shape in the salt solutions than in pure water.

In the second step, a further difference was calculated between the two difference spectra obtained in the first step as shown in Figs. 1c, d and e. The spectrum (Fig. 1d) of HDO in the bulk water, $X(\nu_i)$, was thereby multiplied by a preliminary scale factor. This final difference spectrum $Y_{\text{obs}}(\nu_i)$ given in Fig. 1e was then subjected to a band-shape analysis using a calculated spectrum of the form: $Y_{\text{calc}}(\nu_i) = \sum c_j \exp(-(\nu_i - \nu_j^0)^2/2a_j^2) + k_1 + k_2\nu_i + k_3X(\nu_i)$.

In this expression k_1 and k_2 are constants defining a baseline; k_3 is a scale factor; c_j , a_j and ν_j^0 are parameters of gaussian bands where c_j is the band height, a_j is the band width and ν_j^0 is the position of the band centre. The parameters k_1 , k_2 , k_3 , c_j , a_j and ν_j^0 could be refined in a least-squares procedure. The function minimized was

$$\phi = \sum_i [Y_{\text{obs}}(\nu_i) - Y_{\text{calc}}(\nu_i)]^2 / |Y_{\text{obs}}(\nu_i)|,$$

the Y 's are absorbance values and the summation is made over the interval 2900–1800 cm^{-1} with a step-length of 1 cm^{-1} .

The choice of gaussian bands was based on an analysis of the OD-band of HDO in pure water. We could confirm earlier results⁵ that the band could be represented by three gaussian components (Fig. 2). In our calculation, the band centres were obtained at 2643, 2506 and 2329

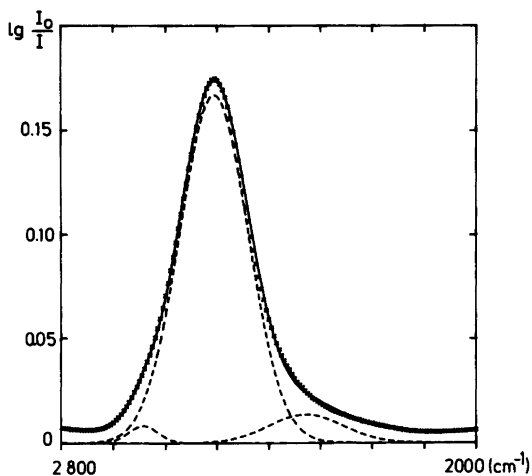


Fig. 2. Calculated (from the band-shape analysis) and measured (dotted) OD stretching band from 2% HDO molecules in water. The measured spectrum corresponds to the one in Fig. 1d. The gaussian components are also shown.

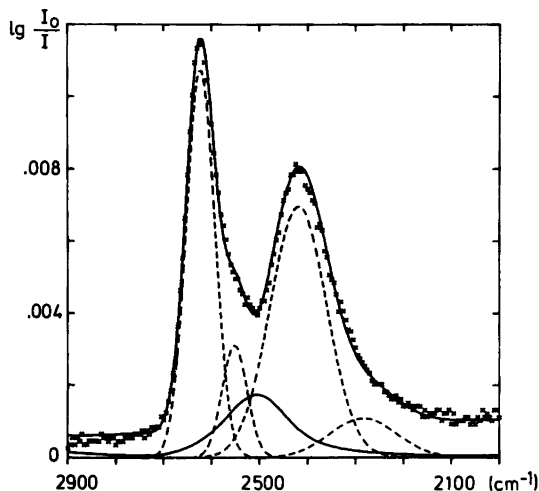


Fig. 3. Calculated and measured difference infrared absorption spectra of a 0.400 molal $\text{Fe}(\text{ClO}_4)_2$ solution containing 2% HDO (See Fig. 1e). The measured spectrum is indicated by crosses at an interval of 5 cm^{-1} . Results from the band-shape analysis is shown from the full curve and the gaussian components (dashed contours). A background HDO band from water on a reduced scale is also shown for comparison (see text).

cm^{-1} , and the component areas were 1.9, 90.1 and 8.0% of the total band area.

The description of the bands as sums of gaussian components is here used as a convenient way of describing the slightly asymmetric bands involved. Work on the use of bands with asymmetric shapes is in progress, however.

In the difference spectrum (Fig. 1e), two main bands are visible. The central parts of these were described by gaussian bands in the initial least-squares refinements, where the scale factor k_3 was varied stepwise until the best fit was obtained. The resulting calculated spectrum was compared to the observed and residual absorption was found at the low wavenumber wings of each band. Two additional gaussian bands were included and refined keeping the first two bands fixed. The refinement of the first two bands was then repeated, together with small adjustments of k_3 . It was not possible to refine all parameters simultaneously. The noise level in the difference spectrum is about 3% of the maximum absorbance observed.

The final results for $\text{Fe}(\text{ClO}_4)_2$ are shown in Fig. 3, in which the HDO band of bulk water (on a reduced scale) is also shown for comparison.

Table 1. Band parameters for $\text{Fe}(\text{ClO}_4)_2$. ν_j° is the band position, c_j the band height, a_j the width of the gaussian band and $A_j = a_j c_j \sqrt{2\pi}$ is the band area. Estimated standard deviations are given in parentheses.

Band	ν_j° (cm^{-1})	c_j	a_j (cm^{-1})	A_j (cm^{-1})
1	2623(2)	0.01008(9)	29.7(2)	0.750
2	2552(1)	0.00291(7)	26.0(1)	0.190
3	2419(1)	0.00653(5)	58.7(4)	0.961
4	2284(3)	0.00102(3)	69.5(2)	0.178

The parameters obtained in the refinements are given in Table 1. The standard deviations given in parenthesis after each parameter value are certainly too small since all parameters could not be refined simultaneously. The accuracy of the method will be better illustrated in the subsequent paper, where results from studies on several perchlorates will be presented.

DISCUSSION

Two main bands at 2623 and 2418 cm^{-1} were obtained from the difference spectrum. The one at 2623 cm^{-1} is assigned as originating from HDO molecules hydrogen bonded to the ClO_4^- ions, in accordance with Ref. 3. By exclusion, the band at 2418 cm^{-1} then would be associated with HDO molecules bonded to the Fe^{2+} ions. This assignment is supported by the results on other salt solutions as shown in the next paper (Part II).⁶ It is interesting to note that the hydration band of the Fe^{2+} ion shows a similar deviation from a perfect gaussian shape as the band from HDO in pure water. An additional gaussian band at 2284 cm^{-1} was thus required to give a better fit at the low wavenumber wing. The origin of the band at 2555 cm^{-1} is more uncertain for several reasons. Part of it may be a low wavenumber wing of the hydration band of the ClO_4^- ion and part may be a high wavenumber component to the Fe^{2+} hydration band. This region, which is close to the centre of the HDO band of pure water, would also be where absorption from water molecules situated further away from the ions, but still significantly influenced by them, would accumulate. There would appear to be only a small proportion of such molecules, however, since the area of the 2555 cm^{-1} band is only 10 % of the total spectral area.

To conclude, the method appears to be very useful for the study of hydration of rather diluted solutions; 0.4 molal is not the lower limit. Furthermore, the observed hydration bands provide a direct measure of the influence of the ions on the hydration spheres. In Part II⁶ we will present spectra for a series of ions which are obtained by the present method.

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