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Drawing out the structural information of the first layer of hydrated ions: ATR-FTIR spectroscopic studies on aqueous NH_4NO_3, $NaNO_3$, and $Mg(NO_3)_2$ solutions

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Abstract

ATR-FTIR technique was used to obtain the difference spectra of aqueous NH_4NO_3 $NaNO_3$, and $Mg(NO_3)_2$ solutions, with $NO_3{}^-$ concentrations ranging from 0 to 4.00 mol dm^{-3}. The water monomers weakly hydrogen bonded with $NO_3{}^-$ ions showed a positive peak near at 3565 cm^{-1} for both $Mg(NO_3)_2$ and NH_4NO_3 solutions. The positive peak was shift to ∼3543 cm^{-1} for $NaNO_3$ solutions due to the total contributions of the hydrated $NO_3{}^-$ (∼3565 cm^{-1}) and the hydrated Na^+ (∼3440 cm^{-1}). Compared with perchlorate solutions, the positive peak of nitrate solutions has a red shift of about 20 cm^{-1} and the peak area is about half of that of perchlorate solutions with the same concentrations, indicating that the hydrogen bonding between $NO_3{}^-$ and water monomers is relative stronger than that between $ClO_4{}^-$ and water monomers, and $NO_3{}^-$ has a strict requirement on the orientation of water molecules when hydrogen bonded with water monomers due to its planar structure. The ab initio calculations were used to understand the splitting of the ν_3 band and hydration effect on the infrared activation of the ν_1. The absorbance of ν_{3b}, ν_1 and ν_2 bands, dependent on the type of cations, was observed to departed from Beer low with increasing concentrations, which is considered as the results of the interactions between cations and nitrate ions.

Keywords: FTIR-ATR; Nitrate; Hydration

1. Introduction

The hydration structures of nitrate ions and the interaction between nitrate and metal ions in aqueous solutions have attracted many interests. So far, there is no detailed understanding on the interactions between $NO_3{}^-$ and H_2O as well as on the structures of various ion pairs in aqueous solutions on molecular level. Infrared and Raman spectroscopy has been widely used to study the ion–solvent and the ion–ion interactions in nitrate aqueous solutions because the vibrational spectra of nitrate ions are sensitive to the perturbation of either the solvent environment or the association with cations [1–10]. The symmetry of nitrate plays a major role in determining its spectroscopic frequencies and selection rules. Unperturbed nitrate has a planar structure with D_{3h} symmetry. With respect to the formation of hydrogen bonds between the oxygen atoms of nitrate and the hydrogen atoms of water molecules, there should be a specific requirement on the orientation of the water molecule different from the spherical anions such as $ClO_4{}^-$ and Cl^-. So, the nitrate solutions also provided a felicitous system to study the hydrogen bond network in aqueous solutions.

In the previous works, the hydration structure of $NO_3{}^-$ has more directly been investigated by X-rays diffraction [11–13]. However, this method is considerably difficult to deduce the detailed hydration structure of $NO_3{}^-$. With the time-of-flight neutron diffraction, Kameda et al. [14] determined the hydration numbers and the intermolecular bond distance in 10 mol% $NaNO_3$ solution in D_2O. Waterland et al. [10] has studied the structures of the nitrate–water complexes using resonance Raman spectra.

In addition, attenuated total reflectance (ATR) spectroscopy can also be used to obtain high quality IR spectra

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of aqueous solutions at various concentrations rapidly. And it has been proved to be very efficient to get the information of molecular interactions in aqueous solution [15–22], although the anomalous dispersion (AD) effect exists in the ATR technology [23,24]. According to the works of Max and Chapados [25], the refractive index of the ZnSe crystal rod is far enough above that of water for it to cause only a very small optical aberration in the ATR spectra of aqueous solutions. If the concentration of water in salt solutions is not much different from that of pure water, the difference spectra of aqueous solutions obtained by ATR techniques are directly proportional to the chemical changes of the sample. In this study, ATR-FTIR technique is used to study the aqueous NH_4NO_3, $NaNO_3$, and $Mg(NO_3)_2$ solutions with NO_3^- concentrations ranging from 0 to 4.00 mol dm^{-3}. With the combination of FTIR-ATR spectra and ab initio calculations, we try to obtain more information about the interactions between nitrate and water and between nitrate and Na^+, NH_4^+ and Mg^{2+}.

2. Experimental

Magnesium nitrate, sodium nitrate and ammonium nitrate with analytical reagent grade were dried over P_2O_5. Solutions were prepared with triple distilled water. Baseline horizontal ATR cell (Spectra-Tech Inc., USA) equipped with a ZnSe crystal (making 11 internal reflections) was adopted for the experiments. Because water has a strong absorbance in O–H stretching region, the detected optical signal is very weak after 11 internal reflections. In order to increase signal–noise radio, one-third of the cell was used. The incident beam was at an angle of 45° with respect to the axis of the rod making three internal reflections. Spectra were recorded on a Nicolet MAGNA-IR 560 spectrometer with a wide-band MCT liquid nitrogen-cooled detector and a KBr beam splitter. The spectral resolution was 4 cm^{-1} using a Happ-Genzel apodization function and a non-zero filling. In total 128 scans were accumulated to obtain high signal–noise levels for the final spectra in the spectral rang of 800–4000 cm^{-1}. The background with the water cell was taken before the measurement of each sample, so the difference spectra of nitrate solutions by pure water are obtained directly. The cell was carefully washed by pure water and the solutions of samples before each measurement. All measurements were taken at about 25. The spectra were reproducible to within ±1 cm^{-1}. The structure calculations are performed with the Gaussian 98 package [26]. Geometry optimizations and vibrational frequency calculations on the ground state nitrate–water complexes were performed at the RHF level with the 6-311G++** basis set. A number of difference initial geometries were chosen, with the nitrate anion and water molecules initially constrained to be coplanar. The potential minima found for the planar structures had all real vibrational frequencies, and no new minima were found when starting from nonplanar structures, although we cannot exclude the possibility that nonplanar local minima exist.

3. Results and discussion

3.1. Spectra of H_2O at various concentrations

The ATR-FTIR difference spectra (1500–3800 cm^{-1}) of aqueous NH_4NO_3, $NaNO_3$ and $Mg(NO_3)_2$ solutions at various concentrations by pure water are shown in Fig. 1. From the different spectra of aqueous $Mg(NO_3)_2$ solutions (Fig. 1a), we can see that the absorbance of the two positive peaks, appearing at ~3567 cm^{-1} and ~3079 cm^{-1}, increases with the increase of the concentration of nitrate ions, while the absorbance of a negative peak, appearing at ~3279 cm^{-1}, decreases with the increase of the concentration of nitrate ions. In the different spectra of aqueous $NaNO_3$ solutions (Fig. 1b) and aqueous NH_4NO_3 (Fig. 1c), the absorbance of positive peaks at ~3543 cm^{-1}, ~3566 cm^{-1}, ~3023 cm^{-1} and ~2886 cm^{-1}, and the absorbance of negative peaks at ~3186 cm^{-1} and ~3289 cm^{-1} have similar changing trend with the increase of nitrate concentration. In the region of the bending vibrations of O–H, the absorbance of a positive peak at ~1635 cm^{-1} increases with increasing the concentration in the difference spectra of $NaNO_3$ solutions. Similar increasing of the absorbance of a positive peak at ~1625 cm^{-1} is also observed in the difference spectra of NH_4NO_3 solutions. There are two positive peaks at ~1679 cm^{-1} and ~1629 cm^{-1} for $Mg(NO_3)_2$ solutions, both of them increase with the increase of the concentrations of nitrate.

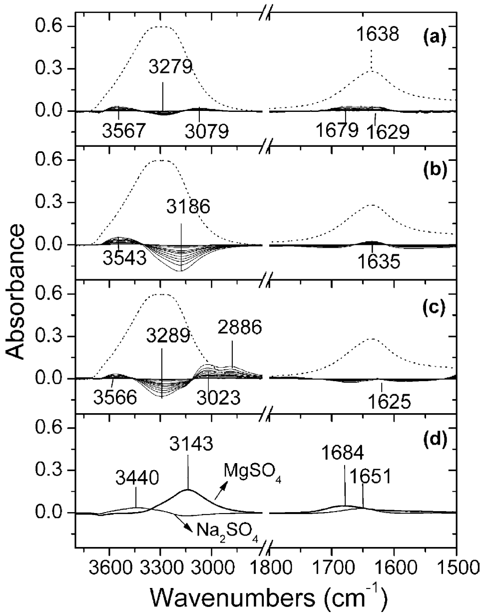

Fig. 1. ATR-FTIR difference spectra (3800–1500 cm^{-1}) of aqueous of (a) $Mg(NO_3)_2$, (b) $NaNO_3$, and (c) NH_4NO_3 solutions at various concentrations by pure water. The concentrations of nitrate anions from dilute to concentrations are 0.10, 0.20, 0.40, 0.80, 1.00, 1.20, 1.60, 2.00, 2.40, 3.00, and 4.00 mol dm^{-3}, respectively. The spectra of pure water are represented by the dotted line. The difference spectra (1500–3800 cm^{-1}) of aqueous $MgSO_4$ and Na_2SO_4 solutions with the same concentration of SO_4^{2-} (2.00 mol dm^{-3}) are shown in part (d).