THE DYNAMIC STRUCTURE OF THE SULFATE ION IN AQUEOUS SOLUTION STUDIED BY RAMAN BANDSHAPE ANALYSIS

D. Watanabe and H. Hamaguchi
Department of Chemistry, School of Science, The University of Tokyo
E-Mail: hhama@chem.s.u-tokyo.ac.jp

Keywords: aqueous solution, sulfate ion, bandshape

Abstract: We measured the concentration dependence of the bandshape of the sulfate ion in aqueous solutions accurately, and analysed the change on the basis of the exchange model. Quantitative information about the dynamics of the ion association has been obtained; the average interval and the lifetime of the association are about 10ps and 200fs respectively.

The Raman bandshape of the symmetric stretching mode ($a_1$ mode) of the sulfate ion in aqueous solutions changes with the increase of the salt concentration (Fig.1). This phenomenon has been known for a long time and studied extensively. Without any interaction among the ions, such change should not occur. Therefore the change has been considered to be the result of the ion association between the sulfate ion and the counter cation. Up to now, this phenomenon has been explained by assuming a static equilibrium, and the observed Raman band has been divided into some components attributed to the species involved in the equilibrium; for instance the free sulfate ion, the contact ion pair, and solvent separated ion pairs. However, our past study suggests that the $a_1$ band of magnesium sulfate in an aqueous solution is homogeneously broadened rather than a superposition of more than one component [1]. Here, we propose a new dynamic exchange model shown in Scheme 1. This scheme expresses the situation that the sulfate ion transforms between the free ion and the associated ion with certain probabilities. It follows that the instantaneous frequency of the sulfate ion exchanges stochastically. Such exchange of frequency causes dephasing and gives width to the band. The bandshape that should be observed in this situation was given theoretically by Anderson [2]. Therefore by fitting the observed bandshape with the theoretical formula, we can obtain information about the dynamics of the ion association under the exchange model. The exchange dephasing is not the only origin of dephasing in solution. Some other causes, mainly the motion of the solvent molecules, make the correlation function decay. The width resulting from such origins is represented by $\Gamma_0$ in Scheme 1.

The concentration dependence of the Raman band of magnesium sulfate in aqueous solutions is shown in Fig.1. We need to fit the spectra with the theoretical formula, but the formula is too complicated and has too many degrees of freedom to obtain meaningful results by a direct fitting. We make an approximation to reduce the number of degrees of freedom. We consider the asymmetric exchange limit in which the ion association is very rare and the sulfate ions stay most of the time as free ions — in other words, the case of very dilute solutions. Details of this approximation are given in Ref. 3. Under this approximation, the bandshape becomes a Lorentzian that is slightly modified from the original one that should be observed in the case when the ion association does not occur. The peak position and the bandwidth change slightly from the original ones, $\omega_1$ and $\Gamma_0$. The peak shift ($\Delta\Omega$) and the increase of the bandwidth ($\Delta\Gamma$) are proportional to each other, and the slope is given as $\tau = (\omega_2 - \omega_1)/\omega_2$. The peak position and the bandwidth obtained by a Lorentzian fitting are shown in Fig.2. The values for ammonium sulfate are also shown in Fig.2. It is seen that the peak position moves to the opposite direction. At the limit of zero concentration, no association is expected to occur. Therefore by extrapolating the plot in Fig.2 to zero, we can obtain the values of $\omega_1$ and $\Gamma_0$: $\omega_1 = 981.0 \pm 0.1 \text{ cm}^{-1}$ and $\Gamma_0 = 2.65 \pm 0.1 \text{ cm}^{-1}$. The plot of $\Delta\Gamma$ and $\Delta\Delta\Omega$ calculated using those values is shown in Fig.3. As is expected by our theory, clear proportional relations are observed. This result cannot be explained by the usual equilibrium model and suggests strongly that our model is valid for this system. By linear fittings of the plots in...
Fig. 3, the values of \( \tau \) were determined to be \( 0.74 \pm 0.01 \) for magnesium sulfate and \( -0.41 \pm 0.02 \) for ammonium sulfate. Now we have determined three parameters, namely \( \omega_1 \), \( \Gamma_0 \) and \( \tau \), it is possible to fit the observed spectra by theoretical formula. Actually, we did the fitting for magnesium sulfate using the values determined from the asymmetric exchange limit approximation. As a result, the values of the remaining parameters (\( W_1 \), \( W_2 \), and \( \omega_2 \)) were determined. The frequency of the associated ion (\( \omega_2 \)) was determined to be \( 1000 \pm 3 \text{cm}^{-1} \). This is very close to the value that is reported as the frequency of the contact ion pair of indium sulfate [4]. So the associated ion is likely to be a contact ion pair. From the formation rate (\( W_1 \)) and the dissociation rate (\( W_2 \)), the average interval of the association (\( T_1 \)) and the average lifetime of the associated ion (\( T_2 \)) can be calculated. The value of \( T_1 \) is shown in Fig. 4, which indicates that the association occurs about every 10ps on an average. \( T_2 \) was determined to be roughly 200fs. This extremely short lifetime suggests that the association is like a “collision” rather than the usual sense of ion pair formation.

![Fig. 1. Concentration dependence of the \( a_1 \) band of the magnesium sulfate solution](image1.png)

**References:**