

Raman Spectroscopic Study of the Ion Association of Lithium Sulfate Aqueous Solutions

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

A Raman spectroscopic study of Li_2SO_4 aqueous solutions as function of concentration and temperature was performed. The dynamic properties of the sulfate ions were studied by a band profile analysis of their internal modes using Fourier transform methods. This analysis reveals the perturbation of the SO_4^{2-} vibrations due to ionic interactions. From the $\nu_1(\text{SO}_4^{2-})$ band profile the spectroscopic ionic association constant was calculated in the range from 5 to 80 °C. The large difference found between the values thus obtained for the association constant and the values obtained from macroscopic measurements is interpreted, assuming that Raman spectra reflect only the short-range forces acting on the ions. Using the Bjerrum equation to calculate the contribution for the long-range forces, good agreement is found between the spectroscopic and macroscopic results.

Key words: Raman spectra, Lithium sulfate, Aqueous solutions, Ionic association, Band profile.

Introduction

Lithium sulfate and the LiASO_4 double salts ($\text{A} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$) have received great interest in the last decades, caused by their application as ionic conductors and ferroelectric materials [1–4]. Also, these systems have additional interest because they show interesting phase transitions as function of temperature [5, 6].

Within the general framework of the crystallization behaviour of these salts from aqueous solutions and solvent mixtures with water we are interested in the ionic association process. The formation of ion-pairs in aqueous solutions of sulfates has been widely discussed from different points of view [7–10]. Nevertheless, the major part of these works deals with systems of divalent cations. This is particularly noticeable for spectroscopic studies with few exceptions [11–15].

Vibrational spectroscopy has proved to be a useful technique for investigating the structural properties of aqueous solutions, mainly when these contain polyatomic ions. The results obtained help understanding the physico-chemical properties of concentrated solutions and the nucleation and growth processes of corresponding crystals.

In the present work we analyze in detail the association process in the case of Li_2SO_4 aqueous solution by the changes of the Raman spectra with concentration and temperature.

Experimental

Solutions of Li_2SO_4 were prepared from extra-pure grade reagent and doubly-distilled water. The solutions were checked by measuring the densities and refractive indices. Raman spectra were obtained in the range 10–4000 cm^{-1} with a spectrometer Ramanor HG2S double monochromator coupled to a computer and in the usual 90° scattering configuration.

The 541.5 and 488.0 nm lines of an argon ion laser were used for excitation of the Raman spectra with an incident power on the sample of about 300 mW. The spectral slit-width was 1 cm^{-1} in all cases. The signal-to-noise ratio was improved by accumulating the multiscanned spectra five times. Spectra were recorded in both I_{vv} and I_{vh} configurations, and from these the isotropic and anisotropic spectra were calculated. In the case of the ν_1 mode of SO_4^{2-} (belonging to the T_d point group) the anisotropic part of the Raman tensor is zero and I_{vv} is taken as I_{iso} .

Spectra at different temperatures in the range 1 to 80 °C were obtained on samples thermostated to

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$\pm 0.1^\circ\text{C}$ in fused silica cells using a circulating water bath.

Results and Discussion

The detailed analysis of the vibrationally averaged structure (V-structure) of aqueous solutions needs the consideration of the internal vibrations of the solvent, the internal vibrations of the solute and all the intermolecular modes. Of particular interest are the cation-water vibrations, which can be interpreted as internal vibrations of aquacomplexes if the water molecules remain much longer in the vicinity of the cations than the average life-time of the hydrogen bond.

We deal with vibrations related to ionic association here, while a study of the internal and external vibrations of the solvent will be published elsewhere.

Figures 1 and 2 show the concentration dependence of the Raman spectra of Li_2SO_4 aqueous solutions over the spectral range $40\text{--}1800\text{ cm}^{-1}$. These include the internal modes of the sulfate ion $\nu_1(\text{A}_1) = 981\text{ cm}^{-1}$, $\nu_2(\text{E}) = 451\text{ cm}^{-1}$, $\nu_3(\text{F}_2) = 1100\text{ cm}^{-1}$, and $\nu_4(\text{F}_2) = 618\text{ cm}^{-1}$ [16], the librational modes of water molecules as well as the low frequency region in which the so-called roto-translational modes of the polyatomic ions and water molecules are located. The

bending mode of water is also included for comparison.

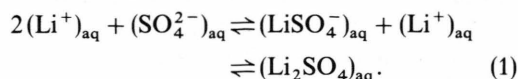
Among the internal modes of SO_4^{2-} , the ν_1 mode exhibits the main changes. A "blue" shift of the band maxima and an increase in the asymmetry of the band profile on the high wavenumber side are observed as the concentration rises. These changes can be interpreted as a progressive weakening of the sulfate-water interaction due to the cation-sulfate perturbation, and it can be related to the ionic association.

In the case of sulfates of divalent cations (mainly Mg^{2+} and Zn^{2+}), the quantitative analyses of these modifications were performed mostly in [11–14] using curve resolving programs in which the band parameters for the possible components were calculated under the criteria of the best fitting consistent with a meaningful model.

In [17] we have underlined the importance of a detailed band profile analysis for the interpretation of the asymmetry or the shoulders occurring in the $\nu_1(\text{SO}_4^{2-})$ band. In general, the key is to decide whether a band is intrinsically asymmetric or the sum of some symmetrical components. In the latter case additional methods for the estimation of band parameters without any previous assumptions are necessary. Among different possibilities we have successfully used Fourier transform methods, i.e. the analysis on the time domain of the appropriate correlation function and self-deconvolution methods [18]

In the case of Li_2SO_4 aqueous solutions the choice between an intrinsically asymmetric profile and a combination of symmetric profiles for the $\nu_1(\text{SO}_4^{2-})$ band is not so clear. Nevertheless, we will use this last interpretation. Figure 3 shows the self-deconvolution of the $\nu_1(\text{SO}_4^{2-})$ profile for a 2.5 m Li_2SO_4 solution. Three components appear at 971, 981 and 988 cm^{-1} . The first component, which has been found in many sulfates of monovalent and divalent cations, is assigned to the ^{18}O isotope fraction of SO_4^{2-} , in agreement with [13]. The 981 and 988 cm^{-1} bands are assigned to the "spectroscopically" non-associated and associated sulfate ions, respectively.

Then we can propose for the association of the ions in Li_2SO_4 solutions the equation in two steps



If the extent of the association is small, $(\text{Li}_2\text{SO}_4)_{\text{aq}}$ can be ruled out. Given the concentration of the solu-

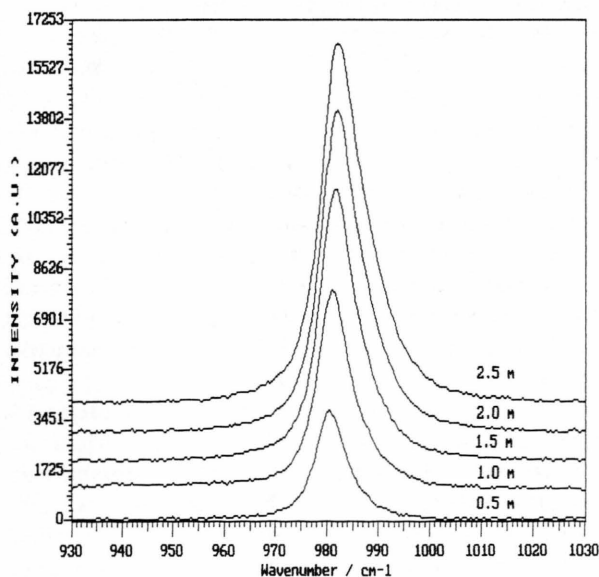


Fig. 1. Raman spectra of the $\nu_1(\text{SO}_4^{2-})$ mode of Li_2SO_4 in aqueous solutions at 25°C as a function of concentration.

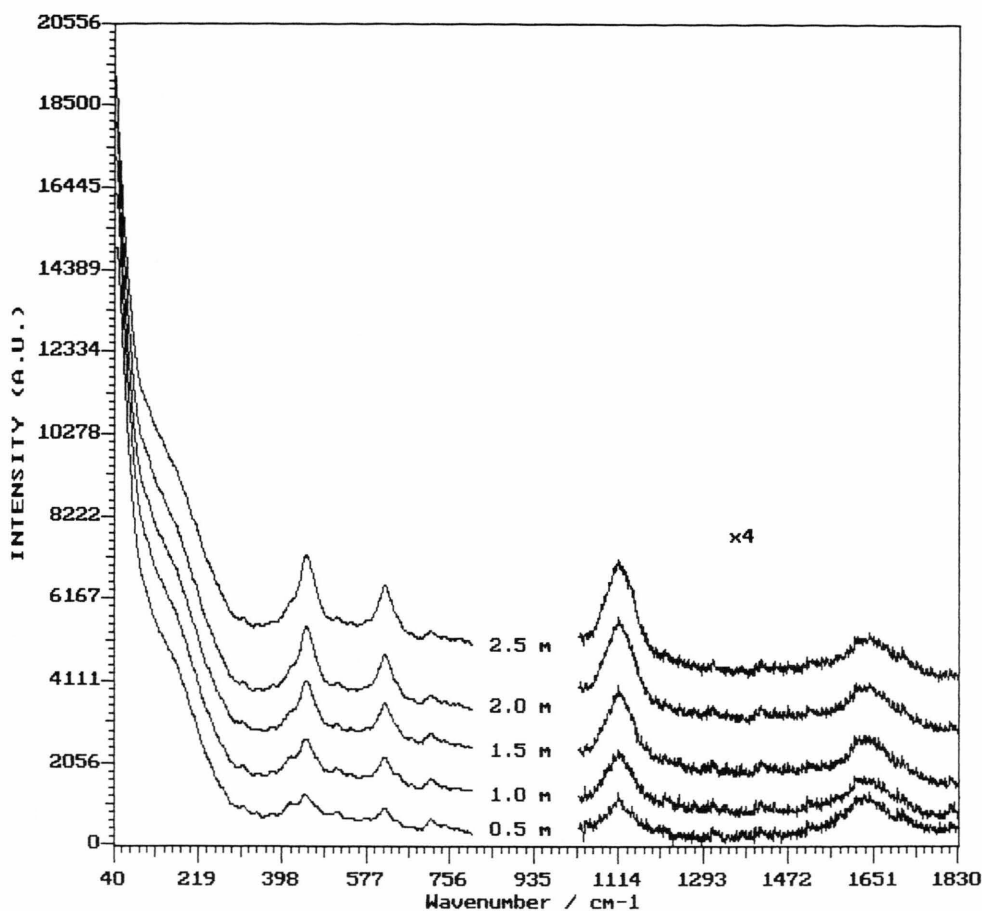


Fig. 2. Raman spectra of Li_2SO_4 aqueous solutions at 25°C as a function of concentration in the spectral region corresponding to the intermolecular motions of water and ions as well as to the internal modes ν_2 , ν_3 , and ν_4 of sulfate.

tion in molalities and assuming α the fraction of dissociated sulfate ions, the association constant of the above reaction can be calculated as

$$K_{\text{ass}} = \frac{1 - \alpha}{\alpha(1 + \alpha)m} \frac{\gamma_{\pm 11}^2}{\gamma_{\pm 12}^3}. \quad (2)$$

Here $\gamma_{\pm 11}$ is defined as the mean activity coefficient of the completely dissociated electrolyte in the first step of (1), $\gamma_{\pm 12}$ relates to the second step of (1) and m is the molality. Since data for $\gamma_{\pm 11}$ are not available, we assume $\gamma_{\pm 11}^2 = \gamma_{\pm 12}^2$ [19]. For simplicity, in (1) $Q_c = (1 - \alpha)/\alpha(1 + \alpha)m$ and $Q_a = 1/\gamma_{\pm 12}^2$.

Now α and $1 - \alpha$ are calculated, respectively, as I_{981}/I_{total} and I_{988}/I_{total} by a computer least-squares fitting method using as input the spectral parameters obtained from the self-deconvoluted spectra. I_{total} is

taken as the integrated intensity in the $930\text{--}1030\text{ cm}^{-1}$ region. It is assumed in this calculation that the sulfate ion has the same molal intensity in the associate and non-associate situation and the integrated intensity is proportional to the concentration. This last statement can be verified (Fig. 4) when the observed intensity is corrected by the local field factor $L_n = 81/(n^2 + 2)^4$, where n is the measured refractive index.

Then we calculated Q_c and $K_{\text{ass}}(\text{sp})$ for each concentration in the range $0.1\text{--}2.5\text{ m}$ (Fig. 5), where the values for Q_a were taken from [8]. We obtained an average value of $K_{\text{ass}}(\text{sp}) = 1.24 \pm 0.06$ at 25°C . This value is considerably lower than the value obtained from macroscopic measurements $K_{\text{ass}} = 5$ [19]. The difference is due to the fact that Raman spectra reflect only the short-range interactions acting on the sulfate

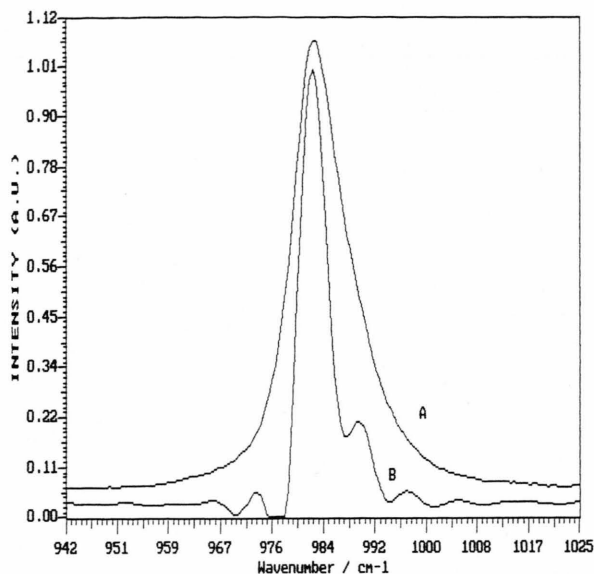


Fig. 3. Experimental (A) and enhanced (B) spectra of the ν_1 band of SO_4^{2-} in a 2.5 m aqueous solution at 25°C. The deconvolution parameters in the time domain are: resolving factor $R = 3.5$, apodization factor $A = 10$ (see [18]).

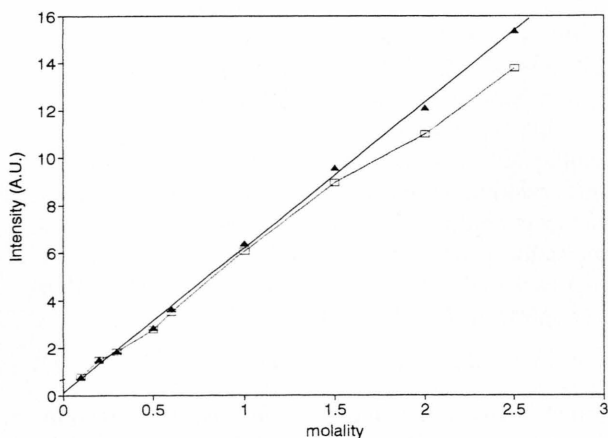


Fig. 4. Plot of the integrated intensity of the $\nu_1(\text{SO}_4^{2-})$ band versus Li_2SO_4 concentration. \square – Experimental, \blacktriangledown – the local-field corrected data.

ions. The long-range force (mainly electrostatic) should be included in K_{ass} but not in $K_{\text{ass}}(\text{sp})$. A calculation of the contribution of the long-range forces in K_{ass} has been made using the Bjerrum equation [20], and a good agreement with the macroscopic value was found [21].

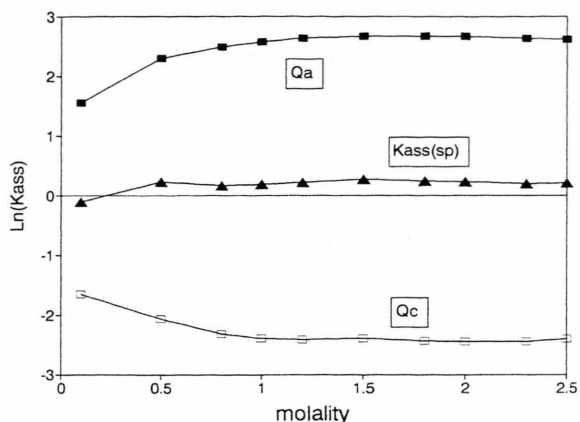


Fig. 5. Dependence of $\text{Ln } Q_c$, $\text{Ln } Q_a$ and $\text{Ln } K_{\text{ass}}(\text{sp})$ at 25°C on salt concentration.

In order to investigate the temperature-dependence of the association process, spectra in the range 5–80°C were taken for 1 m and 2 m solutions. Figure 6 shows the temperature-dependence of the calculated band parameters for $\nu_1(\text{SO}_4^{2-})$ and Fig. 7 shows the temperature-dependence of the association constants Q_c , Q_a , and $K_{\text{ass}}(\text{sp})$.

It is clear that the $\text{Ln } Q_c$ plot is linear in the range studied and that the slightly curved shape shown by $\text{Ln } K_{\text{ass}}$ is due to the behaviour of $\text{Ln } Q_a$. It should be noted that the obtained Q_c -values of the 1 m and 2 m solutions do not differ appreciably. From these data we can calculate the enthalpy and entropy for the association process. The obtained values, averaged for 1 and 2 m, are $\Delta H = 20 \text{ kJ mol}^{-1}$ and $\Delta S = 71 \text{ J mol}^{-1} \text{ K}^{-1}$.

Also the degenerate $\nu_2(\text{E})$, $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$ sulfate modes can be used to ascertain possible changes in the ion symmetry due to ion association. However the ν_2 and ν_4 the spectra are complicated by the presence of water librations as well as possible ion-water bands, in particular the $\text{Li}(\text{H}_2\text{O})_n$ stretching. Disregarding the low frequency part, which can not be analyzed in terms of symmetrical components, the analysis of the band profile shows several polarized bands besides the sulfate ν_2 and ν_4 bands which can be assigned in principle to the librational modes of water [22]. Although the detailed analysis of their behaviour is out of the scope of this paper, the component at 382 cm^{-1} deserves some attention because its position is very close to that found in LiCl aqueous solutions for the stretching Li-water vibration [23].

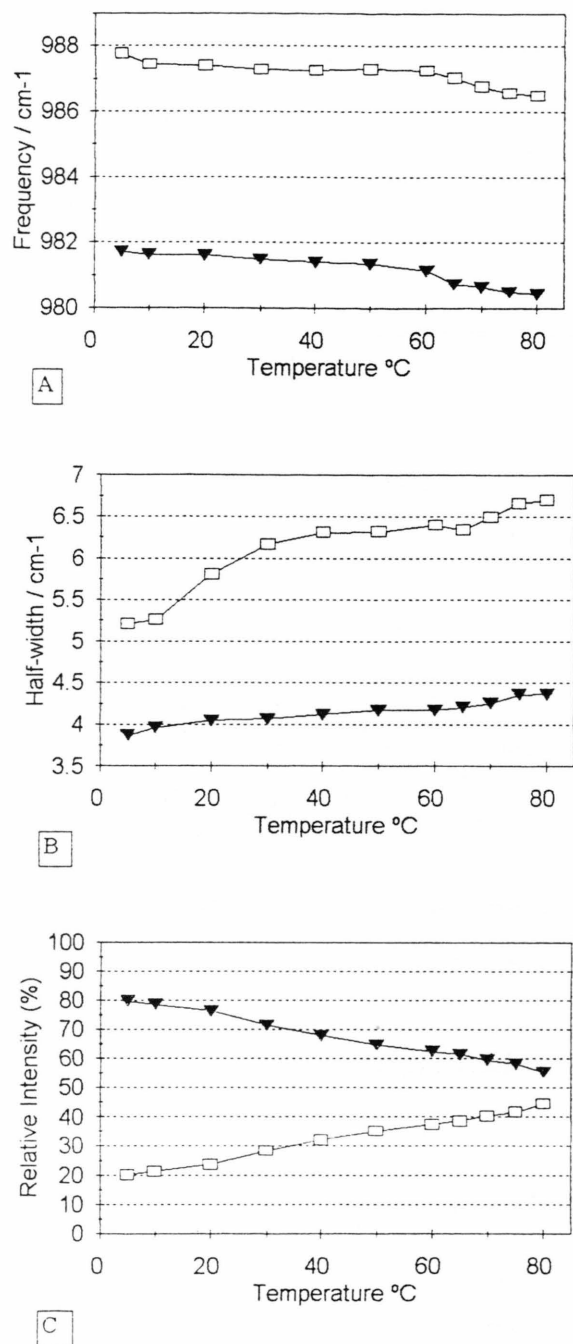


Fig. 6. Changes of the calculated band parameters of the $\nu_1(\text{SO}_4^{2-})$ band with temperature for a 2 m Li_2SO_4 aqueous solution. \blacktriangledown – component at 981 cm^{-1} , \square – component at 987 cm^{-1} .

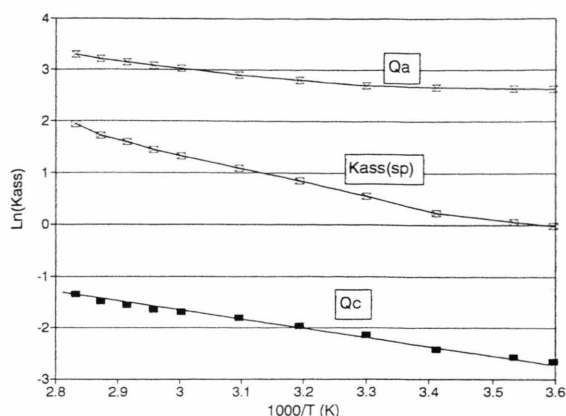


Fig. 7. Plots of $\ln Q_c$, $\ln Q_a$ and $\ln K_{\text{ass}}(\text{sp})$ versus $1/T$ for a 2 m Li_2SO_4 aqueous solution.

It this band belongs to the water-Li motion, its intensity will be related to the Li concentration, i.e. with the sulfate intensity bands and not with the water contents. Here we implicitly assume that the bulk and ion-bounded water molecules show different spectral features which can be separated in the experimental spectra, although this is not in general the case.

Because of the contributions of the broad bands at 180 and 420 cm^{-1} , the fitting of the spectra in this region is not very accurate and a subtraction of the possible contribution from the “bulk-water” spectra should be necessary. Also, to obtain reliable data in this region the estimation of the molar scattering efficiency is needed, which can be related directly to the molecular properties of the different species.

A way to do this is to construct the reduced intensity spectrum $R(\nu)$ [22, 24]

$$R(\nu) = B \ln \nu (\nu - \nu_0)^{-4} I(\nu), \quad (3)$$

where $I(\nu)$ is the experimental intensity, B the temperature factor for which usually a Boltzman distribution is used and \ln the local field correction factor. The $R(\nu)$ spectra also have the advantage to suppress the strong contribution from the Rayleigh scattering.

Now a band profile analysis has been performed on the reduced $R_{\nu\nu}(\nu)$ spectra before and after subtraction of an approximate “bulk-water” spectrum semi-empirically calculated using data for the coordination numbers of the ions from X-Ray diffraction [25] and IR spectroscopy [26].

Figure 8 shows the dependence of the reduced $R_{\nu\nu}(\nu)$ spectra in the region 200 to 800 cm^{-1} on the

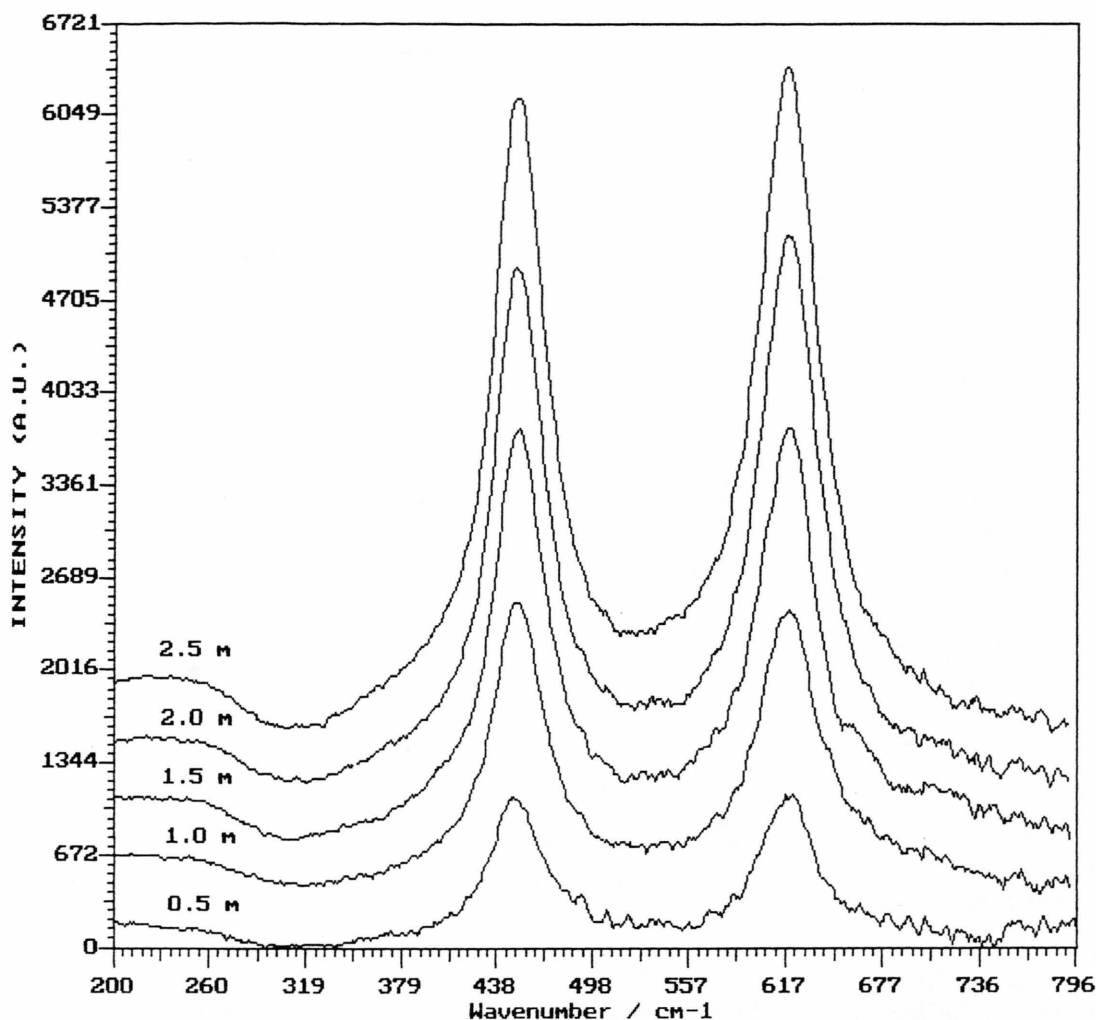


Fig. 8. Concentration effect on the reduced $R_{\nu}(\nu)$ spectra of Li_2SO_4 aqueous solution after subtraction of a calculated "bulk-water" spectrum in the $200\text{--}800\text{ cm}^{-1}$ range.

salt concentration after the subtraction of the "bulk-water" spectra. The original data were also corrected for a linear base-line and filtered using Fourier transform methods. Figure 9 shows the obtained fitting for a 2.5 m aqueous solution.

It is found that with this computer-assisted differential method the bands at 420 and 730 cm^{-1} arising from water librations are practically cancelled, but not the band at 550 cm^{-1} . The ratio between the intensity of the 382 cm^{-1} band and the intensity of the $\nu_2(\text{SO}_4^{2-})$ band is nearly a constant for all concentrations.

Although these results support in principle the assignment of the component at 382 cm^{-1} to the Li-water stretching vibration, work is now in progress to ascertain this through a comparative study of different cations in combination with deuterium/hydrogen isotopic substitution in the solvent.

On the other hand, the ratio between the intensities of $\nu_2(\text{SO}_4^{2-})$ and $\nu_4(\text{SO}_4^{2-})$ in the $R_{\nu}(\nu)$ spectra is close to unity and decreased slightly with concentration. Moreover, this ratio does not depend on the subtraction of the "bulk-water" spectra.

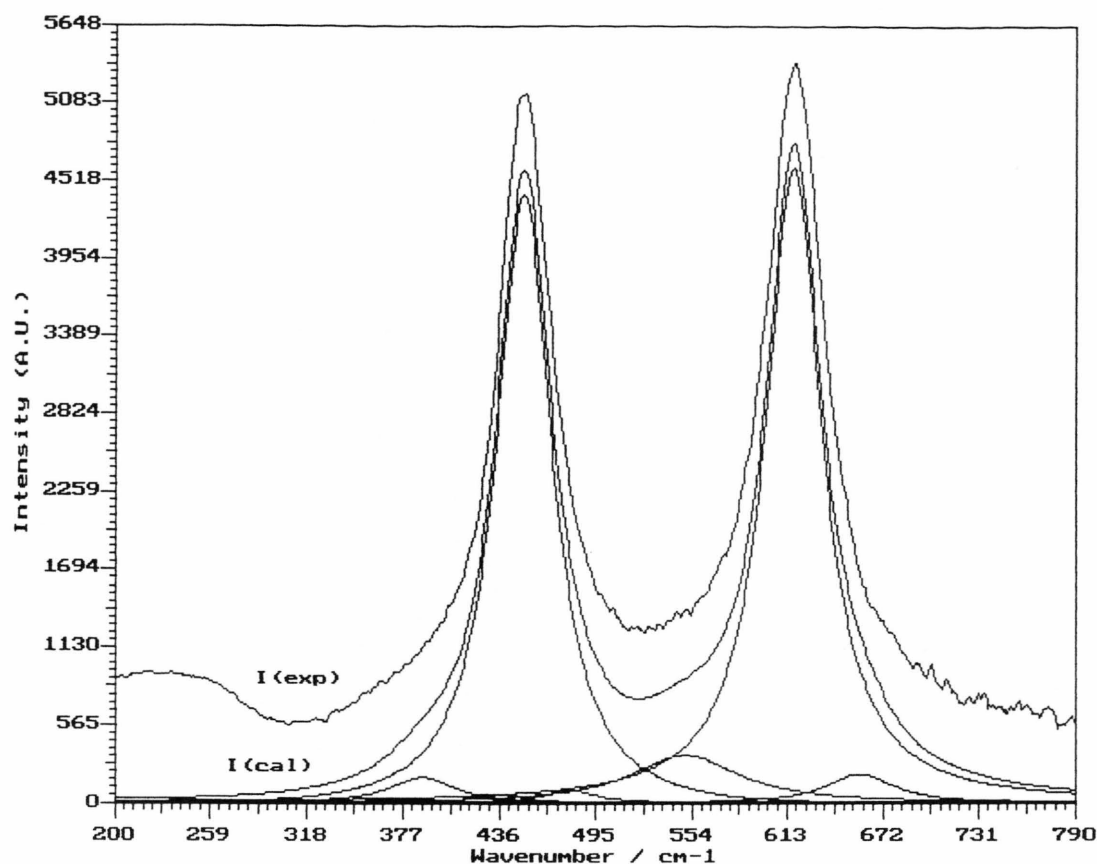


Fig. 9. Curve fitting results for the $R_{vv}(v)$ spectra of a 2.5 m Li_2SO_4 aqueous solution after subtraction of the calculated "bulk-water" spectrum.

Figure 9 shows some asymmetry of the ν_2 and ν_4 bands on the high frequency side which could be separated in terms of symmetrical components. These components are better estimated in the "bulk-water" subtracted spectra and their intensities behave parallel to the ν_2 and ν_4 main components. These results are in our opinion in agreement with those observed in the $\nu_1(\text{SO}_4^{2-})$ band profiles and reflect the sensitivity of the sulfate bending modes to the interaction with the cation.

In a similar way we can expect the $\nu_3(\text{SO}_4^{2-})$ stretching mode to be sensitive to this perturbation. Figure 10 shows the intensity normalized spectra of this band for some selected concentrations and the fitting performed for the 2.5 m solution after a self-deconvolution analysis of the band profile. Three main components appear at positions 1086, 1112, and 1140 cm^{-1} . They maintain their position and also in

a great extent their relative intensity as function of concentration. Any attempt to fit this band with a single component failed despite of the use of any combination of Lorentzian and Gaussian band profiles. This result can be attributed to the fact that the triply degeneracy of the $\nu_3(\text{F}_2)$ mode is partially removed in Li_2SO_4 aqueous solutions as a consequence of the ion association.

Conclusions

Among the internal modes of the sulfate ion the $\nu_1(\text{A}_1)$ and $\nu_3(\text{F}_2)$ modes appear as the most sensitive ones to the ionic association in Li_2SO_4 aqueous solutions.

The self-deconvolution of the $\nu_1(\text{A}_1)$ band profile using Fourier transform methods allows for an esti-

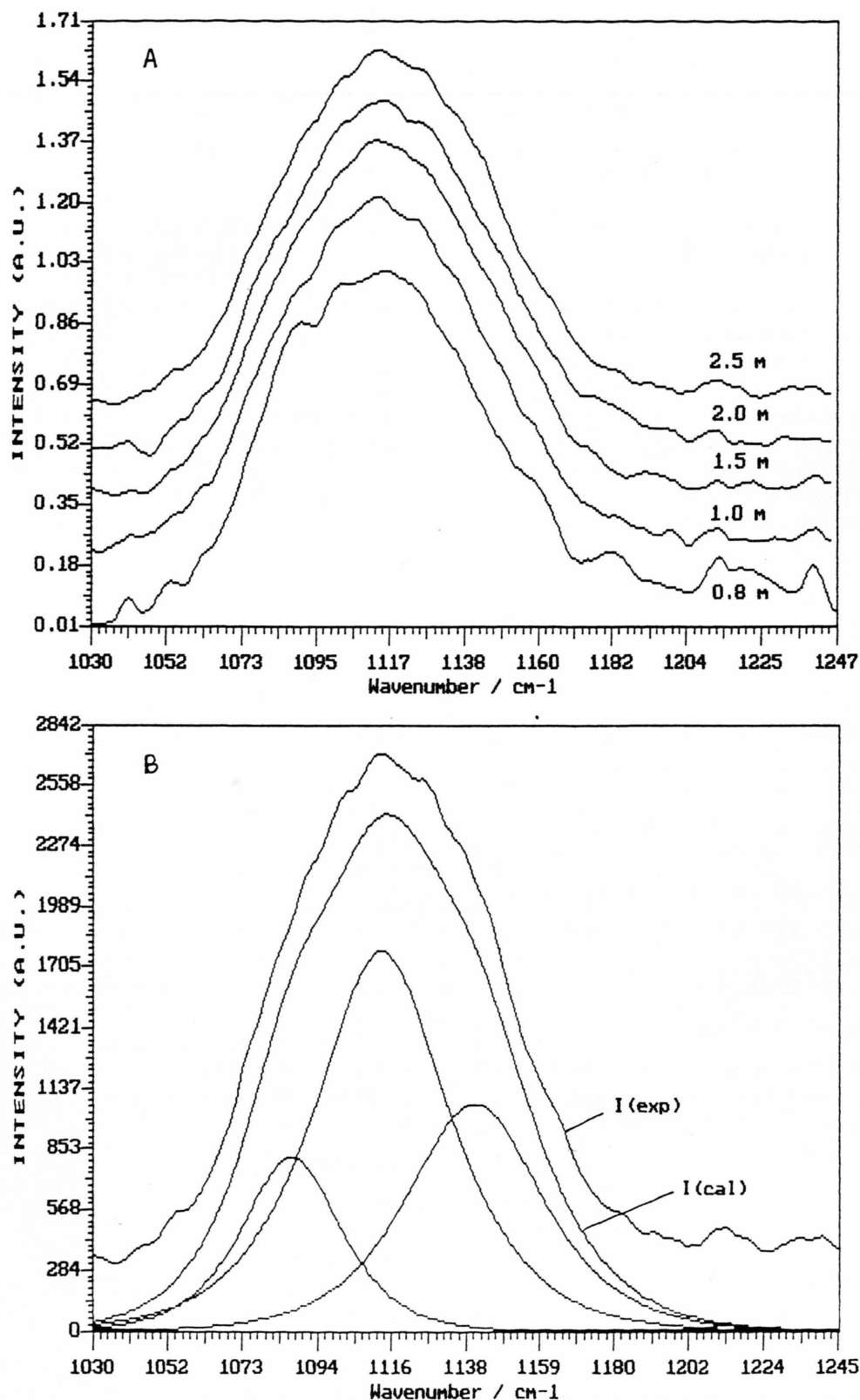


Fig. 10. A) Intensity normalized band profile of the $\nu_3(\text{SO}_4^{2-})$ mode as a function of concentration for Li_2SO_4 aqueous solutions at 25 °C. B) Results obtained from the curve-fitting of the band profile in a solution at 2.5 m.

mation of the number of the possible components under the profile and their band parameters without any previous assumption. In the case of Li_2SO_4 two main components are found in the range of concentration and temperature studied. These are assigned to the "spectroscopically" associated and non-associated fraction of sulfate ion, and from their intensities the spectroscopic association constant has been estimated.

Band parameters are mainly sensitive to the perturbations made by the closest neighbors to a reference molecule or ion. Therefore, the results obtained from the band profile analysis of the $\nu_1(\text{A}_1)$ mode of the sulfate ion can be related to the last step of the ionic association process according to an Eigen and Tamm mechanism. The calculation of the contribution of long-range forces for the consecutive steps in the association process were effectuated using the Bjerrum

equation. Good agreement between the macroscopic and the calculated overall association constant was found.

Finally, results from the band profile analysis in the low-frequency region allow the assignment of the component found at 382 cm^{-1} to the symmetrical $\text{Li}(\text{H}_2\text{O})_n^+$ stretching vibration. It is known that the Li^+ coordination number is concentration dependent [27], however the intensities indicate that the $\text{Li}(\text{H}_2\text{O})_n^+$ complex is stable in the concentration-range studied.

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