Raman spectroscopic investigation of speciation in MgSO$_4$(aq)

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Abstract
Careful measurements have been made of the Raman spectra of aqueous solutions of Mg(ClO$_4$)$_2$, MgCl$_2$, (NH$_4$)$_2$SO$_4$ and MgSO$_4$ down to 50 cm$^{-1}$ and, in some cases, to extremely low concentrations ($\geq$0.0006 mol/kg) and high temperatures ($\leq$200°C). In MgSO$_4$(aq), the well known asymmetry in the $\nu_1$-SO$_4^{2-}$ mode at ~980 cm$^{-1}$ that develops with increasing concentration has been assigned to a mode at 993 cm$^{-1}$ associated with the formation of an MgOSO$_3$ contact ion pair (CIP). Confirmation of this assignment is provided by the simultaneous and quantitative appearance of stretching modes for Mg–OSO$_3$ of the ligated SO$_4^{2-}$ at 245 cm$^{-1}$ and for the (H$_2$O)$_5$MgOSO$_3$ unit at 328 cm$^{-1}$. The CIP becomes the dominant species at higher temperatures. Alternative explanations of the broadening of the $\nu_1$-SO$_4^{2-}$ mode are shown to be inconsistent with this and other Raman spectral evidence such as the similarity of the $\nu_1$-SO$_4^{2-}$ mode for MgSO$_4$ in H$_2$O and D$_2$O. After subtraction of the CIP component at 993 cm$^{-1}$, the $\nu_1$-SO$_4^{2-}$ band in MgSO$_4$(aq) showed systematic differences from that in (NH$_4$)$_2$SO$_4$(aq). This is consistent with a previously undetected $\nu_1$-SO$_4^{2-}$ mode at 982.2 cm$^{-1}$ that can be assigned to the presence of solvent-shared ion pairs (SIPs). In solutions with high Mg$^{2+}$/SO$_4^{2-}$ concentration ratios, a further $\nu_1$-SO$_4^{2-}$ mode was observed at
1005 cm\(^{-1}\), which has been tentatively assigned to a Mg\(_2\)SO\(_4\)\(^{2+}\)(aq) triple ion. All of these observations are shown to be in excellent agreement with recent dielectric relaxation spectroscopy measurements. In addition, the correct relationship between the Mg\(^{2+}/\)SO\(_4^{2-}\) association constant determined by Raman spectroscopic measurements and those obtained by other techniques is derived. It is shown that thermodynamic data measured by Raman spectroscopy for systems involving other (undetected) ion-pair types in addition to CIPs, cannot and should not be compared directly with those obtained by traditional techniques.
1. Introduction

Aqueous solutions of magnesium sulfate are of considerable practical importance as MgSO\textsubscript{4} has significant biological functions [1] and is a major component of seawater, where it is responsible for the high absorption of sound [2,3]. Magnesium sulfate is also present in many natural brines [4,5] and may occur at very high concentrations in environmental aerosols [6].

Not surprisingly therefore, MgSO\textsubscript{4}(aq) solutions have been intensively investigated over a long period of time. Nevertheless, the speciation in this apparently simple system remains surprisingly poorly defined. Of the many techniques employed in the study of MgSO\textsubscript{4}(aq), Raman spectroscopy has undoubtedly been one of the most useful and a number of such investigations have appeared [7-11]. Yet many of the features of the Raman spectra of MgSO\textsubscript{4}(aq), such as the weak SO\textsubscript{4}\textsuperscript{2–} bending modes and the low frequency Mg–O vibrations, remain poorly characterized. Even the interpretation of well-established spectral features, such as the developing asymmetry of the strong ν\textsubscript{1}-SO\textsubscript{4}\textsuperscript{2–} band at ~980 cm\textsuperscript{-1} with increasing MgSO\textsubscript{4} concentration, and their relationship to the speciation in MgSO\textsubscript{4}(aq), has remained highly controversial [7,9-11].

A recent dielectric relaxation spectroscopy (DRS) study, performed over a wide range of concentrations and frequencies, has confirmed that MgSO\textsubscript{4}(aq) is significantly associated[12]. More importantly, that study demonstrated unequivocally, as has long been inferred from ultrasonic absorption (UA) measurements,[13-15] that all three types of ion pair: double solvent-separated (2SIP), solvent-shared (SIP) and contact (CIP), co-exist in such solutions.

In view of the availability of these DRS results[12] and the steady improvements in Raman spectrometers in recent years[16,17] it is timely to make a detailed reinvestigation of the Raman spectra of MgSO\textsubscript{4}(aq). However, to properly interpret such spectra it is essential to first thoroughly characterize the spectra of free (unassociated) Mg\textsuperscript{2+}(aq) and SO\textsubscript{4}\textsuperscript{2–}(aq) ions. This paper therefore presents a detailed analysis of the spectra of MgSO\textsubscript{4}(aq) and also of aqueous solutions of other relevant salts: Mg(ClO\textsubscript{4})\textsubscript{2}, MgCl\textsubscript{2} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and some of their mixtures. In addition, the relationship between the apparent association constant for MgSO\textsubscript{4}\textsuperscript{0}(aq) obtained by Raman spectroscopy and those measured by other techniques is discussed in detail.
2. Experimental details and data analysis

2.1 Solution preparation

All solutions were prepared by weight, unless otherwise specified, from double glass-distilled water and the appropriate salt. Solution densities were measured with a pycnometer (5 mL) at 23 °C. Magnesium concentrations were determined by complexometric titration against standard EDTA [18].

A 2.213 mol/kg stock solution (pH = 6.26) of magnesium perchlorate was prepared from Mg(ClO$_4$)$_2$·6H$_2$O (Alfa Aesar, USA, reagent grade). The corresponding deuterated solution was prepared by dissolving Mg(ClO$_4$)$_2$·6H$_2$O in D$_2$O (Cambridge Isotope Laboratories, UK, 99.9 %). After several partial evaporations, the deuteration level, as determined by Raman spectroscopy, was found to be better than 99.0 %. Three magnesium chloride stock solutions (5.90; 3.48 and 3.30 mol/kg) were prepared from MgCl$_2$·6H$_2$O (Merck, p.a.). A 3.013 mol kg$^{-1}$ magnesium sulfate stock solution (pH = 5.95) was prepared from MgSO$_4$·7H$_2$O (Merck, p.a.). A deuterated 2.093 mol/kg stock solution was formed by dissolving MgSO$_4$·7H$_2$O in D$_2$O. The deuteration level (Raman) after repetitive evaporation was better than 96.0 %. Ammonium sulfate stock solutions were prepared from (NH$_4$)$_2$SO$_4$ (Merck, p.a.). Stock solutions required for the determination of the scattering coefficient of $\nu_1$-MgO$_6$ were prepared from MgCl$_2$·6H$_2$O and NH$_4$ClO$_4$ with the following concentrations (all mol/L): (2.336 MgCl$_2$ + 0.2738 NH$_4$ClO$_4$); 2.487 MgCl$_2$ + 0.1257 NH$_4$ClO$_4$);(2.888 MgCl$_2$ + 0.2478 NH$_4$ClO$_4$).

2.2 Raman spectroscopic measurements

All solutions were filtered through a 0.22 μm Millipore filter into 150 mm i.d. quartz tubes (~1 mL in volume) for Raman measurements. Raman spectra at higher temperatures and a few at room temperature were obtained with a Coderg PHO Raman spectrometer using the 488.0 nm argon ion laser line with a power level at the sample of about 900 mW as described elsewhere[17]. All other Raman measurements were performed at Freiberg using a triple-stage Jobin Yvon monochromator T64000 equipped with a liquid-nitrogen-cooled CCD detector. The spectra were recorded using a 90° scattering arrangement with the 514.5 nm
line of an Ar$^+$-laser at a power level of 800 mW. The spectral resolution was normally 2.0 cm$^{-1}$. However, for the much narrower $\nu_1$ mode of SO$_4^{2-}$, measurements were carried out in the additive mode with a spectral resolution of 0.7 cm$^{-1}$. $I_{\parallel}$ and $I_{\perp}$ spectra were obtained with fixed polarisation of the laser beam by rotating the polarisor at 90° between the sample and the entrance slit to give the scattering geometries:

$$I_{\parallel} = I(Y[ZZ]X) = 45\alpha^2 + 4\gamma^2$$

$$I_{\perp} = I(Y[ZY]X) = 3\gamma^2$$

A program was applied that corrected the measured intensity for the fourth power frequency factor and then set the lowest data point to zero and the highest to 999 on a relative scale. This form of data is defined as the $I(\nu)$ spectrum and should be independent of the excitation frequency. The same program was applied to correct for the fourth power scattering factor, the Bose-Einstein temperature factor, $B = [1-\exp(-h\nu c/kT)]$ and the frequency factor, $\nu$, to give the reduced or $R_Q(\nu)$ spectrum, which is directly proportional to the point-by-point relative scattering activity, $S_Q(\nu)$, in terms of mass-weighted normal coordinates, $Q$, in the double harmonic approximation. $R_Q(\nu)$ is the form of the Raman spectrum that most closely approaches the vibrational density of states [19]. The relationship between the $I(\nu)$ and $R_Q(\nu)$ forms of the spectra is given by eq. (3).

$$S_Q(\nu) \propto R_Q(\nu) = I(\nu) \cdot \nu \cdot B$$

(3)

The normalized isotropic R-spectra were constructed by subtraction:

$$R(\nu)_{iso} = R(\nu)_{\parallel} - 4/3R(\nu)_{\perp}$$

(4)

In the low wavenumber region only the $I(\nu)$ and $R_Q(\nu)$ spectra are significantly different and only the R-format spectra are presented. It should be noted that one of the advantages of using isotropic spectra is that the baseline is almost flat in the wavenumber region of about 320 – 700 cm$^{-1}$ allowing relatively unperturbed observation of any weak modes present.
For quantitative measurements, the perchlorate band, $\nu_1$-$\text{ClO}_4^-$ at 935 cm$^{-1}$ was used as an internal standard. The relative isotropic scattering coefficient $S(\nu_1$-$\text{MgO}_6)$ was obtained from the $R_{\text{iso}}$ spectra. The advantage of $S$ values over $J$ values is that $S$ values can be put on an absolute scale[17]. Further details about the high temperature measurements, the band fitting procedure and $R$-normalized spectra are described elsewhere[17,20].

3. Results and Discussion

3.1 Characterization of unassociated $\text{Mg(OH}_2)_6^{2+}$(aq)

It is generally accepted that, although there may be minor levels of association in aqueous $\text{Mg(ClO}_4)_2$, and $\text{MgCl}_2$ solutions, in neither case does the anion penetrate into the first coordination sphere of the hexaquamagnesium(II) ion. That is, if any association does occur in such solutions only (weak) outer sphere complexes are formed. Such solutions are therefore appropriate for characterizing the spectral features of $\text{Mg(OH}_2)_6^{2+}$(aq).

The isolated $\text{Mg(OH}_2)_6^{2+}$ species possesses $T_h$ symmetry[20,21] so, with its 19 atoms, $3N - 6 = 51$ nmv (normal modes of vibration) are expected and the irreducible representation is: $\Gamma_{\text{vib}}(T_h) = 3a_g + a_u + 3e_g + e_u + 5f_g + 8f_u$. The Raman active modes are $a_g$ (totally polarized) and $e_g$ and $f_g$ (both depolarized). The nmv of $\text{Mg(OH}_2)_6^{2+}$ in the gas phase have been calculated by Pye and Rudolph[20] using $ab\text{ initio}$ methods. In aqueous solution, where the water modes can be considered as decoupled, it is sufficient to consider $\text{Mg(OH}_2)_6^{2+}$ as an $\text{MgO}_6$ unit of $O_h$ symmetry with the water molecules being seen as point masses. The 51 nmv of $\text{Mg(OH}_2)_6^{2+}$ may then be divided into $6 \times 3 = 18$ internal and $6 \times 3 = 18$ external vibrations of the six coordinated water molecules and 15 modes of the $\text{MgO}_6$ unit [23]. The internal modes of the coordinated water molecules include deformation and stretching (at 1650 cm$^{-1}$ and 3000 to 3500 cm$^{-1}$) whilst the external modes are librations (which are weak and broad at around 300 to 800 cm$^{-1}$ [23]). These water modes are outside the scope of this paper and will not be discussed further.

The 15 nmv of the $\text{MgO}_6$ unit span the representation: $\Gamma_{\text{vib}}(O_h) = a_{1g} + e_g + 2f_{1u} + f_{2g} + f_{2u}$. The modes $v_1(a_{1g})$ (polarized), $v_2(e_g)$ and $v_5(f_{2g})$ (both depolarized) are Raman active whilst the $v_3(f_{1u})$ and $v_4(f_{1u})$ modes are IR active and the $v_6(f_{2u})$ mode is not active. The following
assignments of the various modes of MgO$_6$ are based on *ab initio* molecular orbital calculations for Mg(OH)$_2$O$_2^+$ and Mg(OH)$_2$O(OH)$_2$O$_2^+$[11] which, for convenience, are summarized in Table 1.

The isotropic band at 358 cm$^{-1}$ in the Raman spectrum (Figure 1) of Mg(OH)$_2$O$_2^+$ (aq), is assigned to the MgO$_6$ symmetric stretching mode $\nu_1(a_{1g})$. The Raman active $\nu_2(e_g)$ mode is too weak to be observed in solution spectra but can be seen at 315 ± 2 cm$^{-1}$ in the Raman spectrum of MgSO$_4$·7H$_2$O(cr)[23]. The broad depolarized mode at 235 cm$^{-1}$ can be assigned to $\nu_3(f_{2g})$. In the IR spectrum, $\nu_3(f_{1u})$ has been observed at 420 cm$^{-1}$[11,22,23]. The clear differences in the positions of the Raman and IR bands support the assignment of O$_h$ symmetry to MgO$_6$. In MgCl$_2$/D$_2$O solutions, $\nu_1$-Mg(OD)$_2$O$_2^+$ shifts to 342 cm$^{-1}$, which is in reasonable agreement with the expected isotope shift: $\nu_1$-Mg(OH)$_2$O$_2^+ = \sqrt{18.02/20.03} \times (\nu_1$-Mg(OH)$_2$O$_2^+$) = 0.9485 × 357 cm$^{-1}$ = 339 cm$^{-1}$.

With increasing temperature, the position of $\nu_1$-MgO$_6$ in both MgCl$_2$(aq) and Mg(ClO$_4$)$_2$(aq) does not change significantly but broadens noticeably. For example, increasing the temperature of a 1.88 mol/kg Mg(ClO$_4$)$_2$ solution from 23 °C to 125 °C, shifted $\nu_1$-MgO$_6$ from 358 cm$^{-1}$ to 353 cm$^{-1}$ whereas the full width at half height (fwhh) increased from 45 cm$^{-1}$ to 58 cm$^{-1}$. Despite these changes the band symmetry was unaltered, confirming that neither ClO$_4^-$ nor Cl$^-$ penetrate into the inner-sphere of Mg(OH)$_2$O$_2^+$ (aq).

Relative intensity measurements for MgCl$_2$ solutions, using the R$_{iso}$ spectrum with NH$_4$ClO$_4$ as an internal standard, yielded a corrected relative scattering coefficient[11] of $S_h = 0.0065 \pm 0.0005$ for the $\nu_1$-MgO$_6$ mode, relative to $\nu_1(a_1)$-ClO$_4^-$ at 935 cm$^{-1}$. This value is very small and reflects the fact that the electron density between Mg–O is not very high; in inorganic chemistry terms, the bond is mostly ionic. Much higher $S_h(\nu_1$-MO$_6$) values are found for transition metal M(OH)$_2$O$_2^+$ ions: 0.032 for Zn [21], 0.045 for Cd [20] and 0.143 for Hg [20], reflecting an increase in softness (tendency to form covalent bonds) of the metal ions.

### 3.2 Characterization of unassociated SO$_4^{2-}$(aq)
The Raman spectral characteristics of the unassociated \( \text{SO}_4^{2-} \) (aq) ion can be established from measurements on \((\text{NH}_4)_2\text{SO}_4\) (aq) solutions, which are generally thought to be fully dissociated. A recent \textit{ab initio} molecular orbital study that included some Raman spectroscopic measurements of \( \text{SO}_4^{2-} \) hydration has been published by Pye and Rudolph [20].

The unassociated \( \text{SO}_4^{2-} \) (aq) ion has \( T_d \) symmetry and thus nine modes of internal vibration, having the representation: \( \Gamma_{\text{vib}}(T_d) = a_1 + e + 2f_2 \). All vibration modes are Raman active but only the \( f_2 \) modes are IR active.

The following features were observed for a 2.742 mol/kg \((\text{NH}_4)_2\text{SO}_4\) solution Raman spectrum (Figure 2). The \( v_1(a_1) \)-\( \text{SO}_4^{2-} \) mode centred on 979.5 cm\(^{-1}\) (fwhh = 6.95 ± 0.05 cm\(^{-1}\)) is almost totally polarised \( (\rho = 0.003, \text{Figure } 2B) \) whereas the \( v_3(f_2) \)-\( \text{SO}_4^{2-} \) band (not shown) centred on 1110 cm\(^{-1}\) (fwhh \( R_{\text{pol}} = 80 \) cm\(^{-1}\)) and the deformation modes \( v_4(f_2) \)-\( \text{SO}_4^{2-} \) at 617 cm\(^{-1}\) (fwhh \( R_{\text{pol}} = 42 \) cm\(^{-1}\)) and \( v_2(e) \)-\( \text{SO}_4^{2-} \) at 452 cm\(^{-1}\) (fwhh \( R_{\text{pol}} = 35 \) cm\(^{-1}\)) are depolarised. At low frequencies, a broad and very weak mode at \( \sim 190 \) cm\(^{-1}\) (fwhh \( \sim 170 \) cm\(^{-1}\)) is observed in the isotropic spectrum (Figure 2A). This mode is also observable in pure water and has been attributed to OH…O bonded water species.[23] In \((\text{NH}_4)_2\text{SO}_4\) (aq) it may be assigned to the restricted translational mode of the OH…OSO\(_3\)\(^{2-}\) species. The corresponding bending mode of this unit is observable at \( \sim 60 \) cm\(^{-1}\).[23]

The \( v_1 \)-\( \text{SO}_4^{2-} \) band shape is symmetrical in both polarisation arrangements but other band parameters vary slightly with concentration (Figures 3 and 4). For example, at 23 °C for a 2.742 mol/kg \((\text{NH}_4)_2\text{SO}_4\) solution, \( v_{\max} \) shifted to slightly higher wavenumbers as the concentration is decreased, reaching 980.4 ± 0.1 cm\(^{-1}\) at infinite dilution (Figure 4A), whilst, using the narrow spectral slit width of 0.7 cm\(^{-1}\), the fwhh decreased from (6.95 ± 0.05) cm\(^{-1}\) to (5.4 ± 0.1) cm\(^{-1}\) at infinite dilution (Figure 4B). Note that the signal-to-noise ratio for our spectra was excellent \((\geq 500:1 \text{ even at } 0.0184 \text{ mol/kg}) \) and, for example, readily allowed the detection at 965 cm\(^{-1}\) of the \( v_1 \)-\( \text{SO}_4^{2-} \) mode of the isotopomer \( \text{S}^{18}\text{O}^{16}\text{O}_3^{2-} \) (Figure 3 inset), which has a natural abundance of only 0.80 mol\%.

More importantly for the present purposes, the symmetry of the \( v_1 \)-\( \text{SO}_4^{2-} \) mode was independent of the salt concentration over the entire range studied (Figure 3).

With increasing temperature the \( v_1 \)-\( \text{SO}_4^{2-} \) band shifted to lower frequencies and broadened.[17] For example, in a 3.780 mol/kg \((\text{NH}_4)_2\text{SO}_4\) solution \( v_{\max} \) varied smoothly from 979.4 ± 0.1 cm\(^{-1}\) at 23 °C to 977.0 ± 0.1 cm\(^{-1}\) at 200 °C whilst the fwhh increased from
7.10 ± 0.05 cm\(^{-1}\) to 11.0 ± 0.1 cm\(^{-1}\).[17] Although the \(v_1\)-SO\(_4^{2-}\) band shape remained symmetrical up to 200 °C it was not Lorentzian. Thus, at 23 °C the Gauss-Lorentz factor (\(R_{GL}\)) was 0.750 (i.e., there is a 25 % Gaussian contribution to the peak shape) but became more Lorentzian with increasing temperature (\(R_{GL} = 0.905\) at 200 °C).[17] Similar behaviour was also found by Fujita and Kimura [23] who studied the relaxation of \(v_1\)-SO\(_4^{2-}\) in aqueous Na\(_2\)SO\(_4\) and (NH\(_4\))\(_2\)SO\(_4\) solutions at 5 – 80 °C.

3.3 Features of the Raman spectra of MgSO\(_4\)(aq)

The Raman spectra of aqueous solutions of MgSO\(_4\) show many additional features to those of the unassociated SO\(_4^{2-}\)(aq) and Mg(OH\(_2\))\(_6^{2+}\)(aq) modes described above. These are now discussed in detail.

3.3.1 Low frequency region (40 - 800 cm\(^{-1}\))

Significant differences exist between the Raman spectra of (NH\(_4\))\(_2\)SO\(_4\)(aq) and MgSO\(_4\)(aq) in the low-frequency region. However, as has been explained above (and discussed in detail previously[16,17]), to make meaningful measurements in this region it is essential to use R-normalized data, so as to obtain spectra free of the influence of the broad quasi-elastic Rayleigh wing. Figure 5 compares the R\(_\parallel\) spectrum of a 3.013 mol/kg MgSO\(_4\) solution (middle trace) with that of a 3.780 mol/kg (NH\(_4\))\(_2\)SO\(_4\) solution (bottom trace) at 23 °C in the low wavenumber region. Both spectra exhibit the restricted translation mode of OH…OSO\(_3^{2-}\) at ~190 cm\(^{-1}\) along with the SO\(_4^{2-}\) deformation modes \(v_2\) at 452 cm\(^{-1}\) and \(v_4\) at 617 cm\(^{-1}\). However, the latter two bands in MgSO\(_4\)(aq) are broadened relative to (NH\(_4\))\(_2\)SO\(_4\)(aq) due to very weak contributions at 490 ± 10 cm\(^{-1}\) and 645 ± 5 cm\(^{-1}\). Furthermore, in MgSO\(_4\)(aq) the \(v_1\)-MgO\(_6\) mode at 358 cm\(^{-1}\) develops a shoulder at 328 cm\(^{-1}\) and a new polarized mode at 245 cm\(^{-1}\) becomes apparent. All of these features become more pronounced with increasing temperature (Figure 5, top spectrum).

Details at low frequencies, including component decomposition, of the isotropic spectrum of the 3.013 mol/kg MgSO\(_4\) solution are given in Figure 6. Whilst Mg(ClO\(_4\))\(_2\)(aq) at 23 °C (Figure 1) shows only a symmetric \(v_1\)-MgO\(_6\) mode at 358 cm\(^{-1}\), in MgSO\(_4\)(aq) the shoulder at ~328 cm\(^{-1}\) on the \(v_1\)-MgO\(_6\) mode is clearly distinguishable (Figure 6A). The most plausible
The assignment of this component is that it is due to the Mg–OH$_2$ mode of the CIP [(H$_2$O)$_3$MgOSO$_3$], hereafter abbreviated $\nu_1$-MgO$_5$O$^\prime$, for which further details are given below. The penetration of SO$_4^{2-}$ into the first coordination sphere of the Mg$^{2+}$ lowers the MgO$_6$ symmetry, which leads to a shift of the Mg–OH$_2$ symmetric stretch. No splitting is observed because the modes are too broad and overlap strongly. Even better evidence for direct contact between SO$_4^{2-}$ and Mg$^{2+}$ stems from the observation of the Mg$^{2+}$–OSO$_3^{2-}$ vibration mode at 245 cm$^{-1}$. Consistent with increased formation of the CIP at higher temperatures (see Section 3.3.2 below), the component analysis shows that the relative importance of both the 328 and 245 cm$^{-1}$ modes increases with increasing temperature (Figure 6B).

### 3.3.2 Sulfate stretching mode region (800 - 1300 cm$^{-1}$)

The characteristics of the strong $\nu_1$-SO$_4^{2-}$ mode in MgSO$_4$(aq) differ considerably from those observed for the non-associated (NH$_4$)$_2$SO$_4$(aq) solutions (Figures 3, 4 and 7). As has been well established, [7,10,11] at ambient temperatures the $\nu_1$-SO$_4^{2-}$ mode at ~980 cm$^{-1}$ shifts to higher wavenumbers and becomes increasingly asymmetric [24,25] as the MgSO$_4$ concentration rises (Figure 7). The changes in $\nu_{\text{max}}$ and the fwhh in MgSO$_4$(aq) are quantified and contrasted with those for (NH$_4$)$_2$SO$_4$(aq) in Figure 4.

Although there is general agreement about these observations[27], their interpretation has been controversial. Most authors[8,12,20] argue that they arise from CIP formation, which produces an additional $\nu_1$-SO$_4^{2-}$ mode at ~993 cm$^{-1}$ (Figure 8A). Consistent with this assignment, the intensity of the 993 cm$^{-1}$ mode decreases at lower concentrations and is virtually undetectable at ~0.0006 mol/kg (Figure 7). On the other hand, Nomura et al.[26, pp364-5] and later Rull et al. [27,28,29] have suggested that the changes in the $\nu_1$-SO$_4^{2-}$ mode are due to perturbations of the dynamics of water molecules around the sulfate ion.

This explanation can be refuted on many grounds. First, the 993 cm$^{-1}$ band is present in the isotropic spectrum to which only vibrational relaxation processes contribute (i.e., there is no reorientational contribution to $R_{\text{iso}}$ spectra)[30]. Second, as can be seen by comparing Figures 8A and 8B, there are no significant differences in the $\nu_1$-SO$_4^{2-}$ profile, including the contribution from the 993 cm$^{-1}$ mode, for solutions of MgSO$_4$ in H$_2$O and D$_2$O. This would
be most unlikely if the $\nu_1$-SO$_4^{2-}$ mode contained an appreciable contribution from the solvent molecules. Third, DRS, which is particularly sensitive to variations in water molecule dynamics, detects no such changes[12]. Fourth, such effects would be expected to occur in all sulfate-containing electrolytes but they are absent from the Raman spectra of unassociated salts such as (NH$_4$)$_2$SO$_4$(aq) (Figures 3 and 4) and from salts such as Na$_2$SO$_4$(aq)[20] that are associated but that form only 2SIPs &/or SIPs.[31]

In another paper, Rull et al.[10] recognised the presence of the 993 cm$^{-1}$ mode but associated it with some type of SIP. This assignment was based on two considerations. The first was that they did not observe the required changes in the Mg–O stretching mode or in the weak low frequency $\nu_2$- and $\nu_4$-SO$_4^{2-}$ bending modes.[10] The second was that their calculation of the stability constant of MgSO$_4^{0}$(aq) via the Bjerrum equation was higher than the observed value if a CIP was assumed. This interpretation, which has been given currency by several reviewers [29,32], is untenable for a number of reasons.

As shown in Section 3.3.1 above (and elsewhere [11]), although the $\nu_2$- and $\nu_4$-SO$_4^{2-}$ modes do not split, they do show effects consistent with the entry of SO$_4^{2-}$ into the coordination shell of Mg$^{2+}$(aq). Figure 9 plots the integrated intensity of the $\nu$-MgO$\_5$O$'$ component at 328 cm$^{-1}$ against that of the $\nu_1$-SO$_4^{2-}$ component at 993 cm$^{-1}$, in each case normalized with respect to the total envelope for that mode. As required for the assignment of these two bands to the formation of a CIP, there is an excellent correlation ($r^2 = 0.997$) between their normalized intensities. The existence of CIPs rather than SIPs as the “last stage of [the] multistage association process”[10] between Mg$^{2+}$(aq) and SO$_4^{2-}$(aq) is confirmed by the dramatic increase in the $\nu_1$-SO$_4^{2-}$ mode at 993 cm$^{-1}$ with temperature (Figure 10). Thus the small asymmetry in the $\nu_1$-SO$_4^{2-}$ mode at 23 °C becomes a clearly defined shoulder at 75 °C and ultimately the dominant component at 198 °C. Such behaviour would not be expected for SIPs (or water dynamics effects for that matter) but is consistent with increased CIP formation resulting from the weakening of the ion hydration shells with increasing temperature.

It may be added that by assuming SIPs as the final stage of association, Rull et al.[10], who also accepted the presence (as detected by UA techniques[13-15]) of three equilibria in the overall association process, were forced to postulate the formation of a triple solvent-
separated ion pair as the first stage. Such a species has, to the best of our knowledge, never
been identified by any technique in any electrolyte solution; even if it did form, it could
hardly be meaningful in terms of its lifetime. More damaging for this hypothesis, however: a
triple solvent-separated ion pair, which would have a very large dipole moment, should be
readily detected by DRS but is not.[12]

In addition, the suggestion by Rull et al.[10] that the Bjerrum equation can be used to
assess the formation of particular types of ion pairs is unrealistic. This simple electrostatic
model is at best a crude approximation (at least one experienced author[33] has described
association constants calculated via the Bjerrum equation as “fictitious”, which is perhaps a
little harsh). To consider just one aspect of the Bjerrum model: its use of the bulk dielectric
constant ($\varepsilon$) for electrolyte solutions, where dielectric saturation of the solvent in the vicinity
of the ions may lower $\varepsilon$ to a small fraction of its bulk value, removes any quantitative
meaning from the results so produced[34].

3.4 Quantitative analysis of contact ion pair formation in MgSO$_4$(aq)

Given, as shown above, that the 993 cm$^{-1}$ component of the $\nu_1$-SO$_4^{2-}$ mode can be
assigned to CIP formation, it is possible to use Raman spectroscopy to derive an association
constant for this species. This has been done in several studies[7,8,10,20] with the results
being in reasonable agreement with each other. Unfortunately, there has been widespread
misunderstanding about the significance of the constant so obtained[29,35] and in particular
its relationship to other association constants reported in the literature for the same system. It
is appropriate therefore to consider this matter in some detail.

The association between Mg$^{2+}$(aq) and SO$_4^{2-}$(aq) ions is generally thought to occur via a
three step process, often referred to as the Eigen mechanism[13-15], in which the strongly
solvated ions combine initially to form a 2SIP or, in the language of inorganic chemistry, an
outer-outer sphere complex. The two intervening water molecules are then lost successively,
forming SIPS and ultimately CIPs (outer and inner sphere complexes respectively). This
process is summarized in the following reaction scheme:
\[ K_1 \quad K_2 \quad K_3 \]
\[
\text{Mg}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \leftrightarrow \text{Mg}^{2+}(\text{OH}_2)\text{SO}_4^{2-}(\text{aq}) \leftrightarrow \text{Mg}^{2+}(\text{OH}_2)\text{SO}_4(\text{aq}) \leftrightarrow \text{Mg}^{2+}\text{SO}_4^{2-}(\text{aq}) \quad (5)
\]

free aquated ions 2SIP SIP CIP

where \( K_i \) (\( i = 1 \) to 3) are the ‘stepwise’ constants for the designated equilibria.

The overall association constant, \( K_A \), as measured by traditional techniques such as potentiometry or conductivity, corresponds to the equilibrium:

\[
\text{Mg}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \leftrightarrow \text{MgSO}_4^0(\text{aq}) \quad (6)
\]

where \( \text{MgSO}_4^0(\text{aq}) \) refers to all forms of associated \{Mg\( ^{2+} \), \( \text{SO}_4^{2-} \}\) species of 1:1 stoichiometry in aqueous solution (thermodynamics makes no distinction between dissolved species of identical stoichiometry but with differing levels of solvation[36]). It is readily shown, ignoring activity coefficient effects throughout, that \( K_A \) is related to the \( K_i \) values via:

\[
K_A = K_1 + K_1K_2 + K_1K_2K_3 \quad (7)
\]

The \( K_i \) values, determined for example by UA[13-15] and DRS[12], are in good agreement and give values of \( K_A \) that lie well within the spread of reliable results reported in the literature using traditional methods. The equilibrium constant for the association between \( \text{Mg}^{2+}(\text{aq}) \) and \( \text{SO}_4^{2-}(\text{aq}) \) measured by Raman spectroscopy differs from both \( K_A \) and \( K_i \).

Following previous studies[7,10,20] and the description given above, it is assumed that the \( \nu_1-\text{SO}_4^{2-} \) band consists of only two significant components: a ‘free’ \( \text{SO}_4^{2-}(\text{aq}) \) mode at \( \sim 980 \text{ cm}^{-1} \) and the CIP mode at \( \sim 993 \text{ cm}^{-1} \) (Figure 8A). In other words, only CIPs are spectroscopically distinct, in which case it follows that the ‘free’ \( \text{SO}_4^{2-}(\text{aq}) \) mode must include contributions from 2SIP and SIP in addition to that from \( \text{SO}_4^{2-}(\text{aq}) \). That is, the constant measured by Raman spectroscopy, \( K_R \), corresponds to the equilibrium:

\[
\text{Mg}^{2+}(\text{aq}) + \text{‘free’ SO}_4^{2-}(\text{aq}) \leftrightarrow \text{CIP}(\text{aq}) \quad (8)
\]
where ‘free’ sulfate, as detected by Raman spectroscopy, $\left[\text{SO}_4^{2-}\right]_R = \left[\text{SO}_4^{2-}\right] + \left[\text{2SIP}\right] + \left[\text{SIP}\right]$ and thus

$$K_R = \frac{[\text{CIP}]}{[\text{Mg}^{2+}][\text{SO}_4^{2-}]_R} \quad (9)$$

In practice, $K_R$ is formulated in terms of $\alpha$, the spectroscopically-determined fraction of sulfate present as CIPs:

$$\alpha = \frac{I_{993}}{I_{980} + I_{993}} = \frac{[\text{CIP}]}{C_T} \quad (10)$$

where $C_T$ is the total (analytical) concentration of MgSO$_4$. From the equilibrium stoichiometry

$$K_R = \frac{\alpha}{(1 - \alpha)^2 C_T} \quad (11)$$

and thus it follows that:

$$K_R = \frac{[\text{CIP}]}{(C_T - [\text{CIP}])^2} \quad (12)$$

From eq. (5) and the appropriate equilibrium constant expressions:

$$[\text{CIP}] = K_1K_2K_3[\text{Mg}^{2+}][\text{SO}_4^{2-}] \quad (13)$$

Furthermore, in stoichiometric MgSO$_4$(aq) solutions, assuming only 1:1 species are formed, mass balance demands that:

$$C_T = [\text{MgSO}_4]_T = [\text{Mg}^{2+}]_T = [\text{SO}_4^{2-}]_T \quad (14)$$

and

$$[\text{Mg}^{2+}] = [\text{SO}_4^{2-}] \quad (15)$$

Combination of equations (12)-(15) then gives:
\[ K_R = \frac{K_1K_2K_3[Mg^{2+}]^2}{(C_T - K_1K_2K_3[Mg^{2+}])^2} \]  

Combination of the mass balance expressions:

\[ [Mg^{2+}]_T = [Mg^{2+}] + [2SIP] + [SIP] + [CIP] \]  

\[ [SO_4^{2-}]_T = [SO_4^{2-}] + [2SIP] + [SIP] + [CIP] \]

with eq. (7) gives a quadratic expression:

\[ K_A[Mg^{2+}]^2 + [Mg^{2+}][Mg^{2+}]_T = 0 \]

that can be solved algebraically for [Mg^{2+}]. Substitution of the physically meaningful root of eq. (19) into eq. (16) enables calculation of \( K_R \) from the \( K_i \) values (and \( K_A \)). Together, eqs. (16) and (19) define the relationship between \( K_R \) and the stepwise constants \( K_i \) determined by UA or DRS, and the overall association constant \( K_A \) determined thermodynamically. It follows that direct comparison of \( K_R \) with \( K_A \), as has often been made in the literature,[29, 35] is incorrect. Note too that, whilst \( K_R \) can be calculated from \( K_i \) (and \( K_A \)), neither \( K_i \) nor \( K_A \) can be obtained uniquely from a single measurement of \( K_R \).

The equations derived here for the Mg\(^{2+}\)/SO\(_4^{2-}\) system are applicable to any system that involves the formation of, in addition to CIPs, significant amounts of 2SIPs &/or SIPs, and to any technique which, like Raman spectroscopy, detects only CIPs. Thus similar considerations will apply to most types of NMR and UV-vis spectroscopy. It also follows that other thermodynamic quantities such as \( \Delta H \) and \( \Delta S \) that can be derived from the temperature dependence of \( K_R \)[29] are not comparable with those obtained by conventional thermodynamic methods. To put the situation bluntly, equilibrium constants for CIPs derived from Raman spectroscopy in systems containing undetected 2SIPs and/or SIPs are technique-specific. Such constants are not comparable with those obtained by thermodynamic techniques and cannot for example be used in speciation calculations. For this reason no such parameters are derived from the present Raman data.
Regardless of the complicated relationship between $K_R$, $K_A$ and $K_i$, it is noteworthy that both Raman spectroscopy and DRS detect CIPs directly, so it is possible to make a quantitative comparison between them. Figure 11 shows the present Raman results (expressed as the fraction of $SO_4^{2-}$ present as CIPs: $\alpha = [\text{CIP}] / [SO_4^{2-}]_T = I_{993}/ (I_{993} + I_{980})$ and noting that the scattering coefficients for bound and free sulphate are equal) as a function of $[MgSO_4]_T$ and compares them with those obtained by DRS[12]. Given the likely uncertainties in both sets of data the agreement is excellent and provides further evidence that the 993 cm$^{-1}$ mode is indeed due to CIPs.

3.5 Detailed interpretation of the $v_1$-$SO_4^{2-}$ band shape

To quantify the degree of CIP formation in Section 3.4 it was assumed that the $v_1$-$SO_4^{2-}$ mode consisted of only two components: one at $\sim$980 cm$^{-1}$ associated with ‘free’ $SO_4^{2-}$ and the other at $\sim$993 cm$^{-1}$ associated with CIPs. On this basis, and consistent with the generally accepted view that, when using only ligand vibrations, 2SIPs and SIPs are indistinguishable from the unassociated ion,[37] it would be expected that subtraction of the CIP contribution from the $v_1$-$SO_4^{2-}$ envelope would produce a mode with characteristics similar to those observed for $v_1$-$SO_4^{2-}$ in solutions of an unassociated salt such as $(NH_4)_2SO_4$. However, when this decomposition is performed, the ‘free’ $SO_4^{2-}$ mode in MgSO$_4$(aq) shows systematic differences from that observed for $(NH_4)_2SO_4$(aq). In particular (Figure 4), the $v_1$-$SO_4^{2-}$ mode in MgSO$_4$(aq) at $\sim$980 cm$^{-1}$, after removal of the 993 cm$^{-1}$ component, shows changes in position and fwhh with increasing concentration that are of much greater magnitude and, in the case of $v_{\text{max}}$, in the opposite direction to those of $v_1$-$SO_4^{2-}$ in $(NH_4)_2SO_4$(aq). These effects are small ($\Delta v_{\text{max}} \leq 2$ cm$^{-1}$; $\Delta$fwhh $\leq 2.5$ cm$^{-1}$) but they are reproducible; similar changes have recently been reported using an FT Raman spectrometer[12]. Importantly, in very dilute solutions (Figures 3, 4 and 7) the shape and location of the $v_1$-$SO_4^{2-}$ mode in MgSO$_4$(aq) and $(NH_4)_2SO_4$(aq) become identical. These features, along with the very narrow slit widths employed and the quality of the present spectra, make it highly unlikely that these observations are artefactual.

In aqueous solution, the sulfate modes are influenced by the environment (environmental broadening). Whilst there is probably a continuum of perturbing environments, it can be assumed that there are preferred energy minima within this continuum. These minima can be
interpreted as corresponding to ion pairs. Thus, the most straightforward explanation for these effects is that the ‘free’ $\text{SO}_4^{2-}$ mode at $\sim 980 \text{ cm}^{-1}$ overlaps with another mode centred at slightly higher wavenumbers. It seems both plausible and chemically reasonable to assign this extra mode to the presence of SIPs. Although (and as discussed above) it is generally thought [37] that Raman spectra involving anion vibrations can distinguish only between ‘free’ anions and those involved in direct bonding to cations (CIPs), James and Frost [38,39] have detected both CIPs and SIPs in their Raman studies of weak metal ion/nitrate complexes in aqueous solutions. Their assignment was based on a Fourier transform procedure for signal narrowing and subsequent band fitting, and assumed that the peak positions of the ‘free’ nitrate and the nitrate in the SIPs and CIPs were virtually independent of concentration. The other sulfate modes also show effects consistent with the formation of SIPs. Thus, the restricted O–H…OSO$_3^{2-}$ stretching mode at $\sim 190 \text{ cm}^{-1}$ in 2 mol/L $\text{MgSO}_4(\text{aq})$ is much broader ($\text{fwhm} \approx 205 \text{ cm}^{-1}$) than in 2 mol/L $(\text{NH}_4)_2\text{SO}_4(\text{aq})$ ($\text{fwhm} \approx 175 \text{ cm}^{-1}$) and $\nu_2$- and $\nu_4$-$\text{SO}_4^{2-}$ in $\text{MgSO}_4(\text{aq})$ are broadened compared with $(\text{NH}_4)_2\text{SO}_4(\text{aq})$ (Figure 5).

Although the above assignment appears reasonable, an unambiguous decomposition of the ‘free’ $\nu_1$-$\text{SO}_4^{2-}$ band (after subtraction of the 993 cm$^{-1}$ mode) is difficult because of the close proximity of the components. The fitting procedure employed was based on considerations similar to those used by Frost and James [38,39]. As the effects of SIP formation on $\nu_1$-$\text{SO}_4^{2-}$ were very much less than those of CIP formation, it was assumed that 2SIPs would not be Raman-distinguishable from $\text{SO}_4^{2-}(\text{aq})$. The total $\nu_1$-$\text{SO}_4^{2-}$ mode was then fitted with the minimum number of components that produced concentration-independent band parameters, except for the intensity. The concentrations of CIPs, SIPs and \{2SIP + $\text{SO}_4^{2-}(\text{aq})$\} derived from the present decomposition of the $\nu_1$-$\text{SO}_4^{2-}$ mode along with the corresponding values determined from DRS measurements are plotted in Figure 12. Given the number of species involved, the probable experimental errors, and the uncertainties with regard to the decomposition of the overlapping bands in both techniques, the level of agreement is very gratifying.
3.6 Spectra at high \([\text{Mg}^{2+}]_T/[\text{SO}_4^{2-}]_T\) ratios

Most Raman spectroscopy on the \{Mg\textsuperscript{2+} + SO\textsubscript{4}\textsuperscript{2-} + H\textsubscript{2}O\} system has been made using solutions prepared directly from magnesium sulfate in which the Mg\textsuperscript{2+}/SO\textsubscript{4}\textsuperscript{2-} concentration ratio is necessarily 1:1. Recently, qualitative evidence was obtained for an additional feature in the \(\nu_1\)-SO\textsubscript{4}\textsuperscript{2-} mode in solutions with very high \([\text{Mg}^{2+}]_T/[\text{SO}_4^{2-}]_T\) ratios\cite{12}. Figure 13 shows the Raman spectrum in the \(\nu_1\)-SO\textsubscript{4}\textsuperscript{2-} region for a solution containing 0.0956 mol/L MgSO\textsubscript{4} and 3.670 mol/L MgCl\textsubscript{2} at 23 °C. Consistent with the previous findings\cite{12} but much more easily discernible in the present higher quality spectra, an additional feature is clearly present at \(\sim\)1005 cm\textsuperscript{-1}. Comparable results (not shown) were obtained under a variety of conditions and a similar feature has also been detected by FT Raman microscopy on highly supersaturated MgSO\textsubscript{4}(aq) droplets \cite{6,40}. The present results are insufficient to unambiguously assign this mode but, consistent with the DRS data\cite{12}, it can probably be assigned to the formation of a (contact) triple ion Mg\textsubscript{2}SO\textsubscript{4}\textsuperscript{2+}(aq) (‘TI’), in which the SO\textsubscript{4}\textsuperscript{2-} directly bonds to (i.e., bridges) two Mg\textsuperscript{2+} ions. Other possibilities include the formation of a bidentate CIP or larger Mg\textsuperscript{2+}, SO\textsubscript{4}\textsuperscript{2-} clusters\cite{6,40}.

4. References and notes

22) The value of 310 cm$^{-1}$ reported for $\nu_3(f_{1u})$ in MgSO$_4\cdot$7H$_2$O(cr) by Nakagawa and Shimanouchi [23] is almost certainly incorrect. Careful inspection of the published IR spectrum[23] shows a weak mode at ~400 cm$^{-1}$.
24) Earlier reports [9, 25] of a symmetrical $\nu_1$-SO$_4^{2-}$ band in MgSO$_4$(aq) are incorrect. Such observations reflect the swamping of the relatively small asymmetry by band broadening due to the large (10 cm$^{-1}$) slit widths then commonly available.
41) The $R_{iso}$ profile of the $v_1$-$SO_4^{2-}$ mode has been taken from the $R_{||}$ spectrum [33] because of the very low contribution from the anisotropic scattering. However, in aqueous solutions the water background has to be taken into account because $v_1$-$SO_4^{2-}$ is sitting on edge of the rocking mode of water (ca. 870 cm$^{-1}$). Use of the $R_{iso}$ profile has the advantage that the scattering contribution of the water is partially removed.
Table 1. MgO₆ skeleton modes (O₆ symmetry) of the Mg(OH₂)₆²⁺ cation. Experimental wavenumbers and calculated wavenumbers (unscaled) in aqueous solution.

<table>
<thead>
<tr>
<th>Assignment and activity of mode</th>
<th>Experimental wavenumbers (cm⁻¹)</th>
<th>Calculated wavenumbers (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ι₁(a₁g), R</td>
<td>357.5 ± 0.5</td>
<td>356</td>
</tr>
<tr>
<td>ι₂(e₂g), R</td>
<td>315 ± 2</td>
<td>334</td>
</tr>
<tr>
<td>ι₃(f₁u), IR</td>
<td>420 ± 2</td>
<td>449</td>
</tr>
<tr>
<td>ι₄(f₁u), IR</td>
<td>-</td>
<td>113</td>
</tr>
<tr>
<td>ι₅(f₂u), R</td>
<td>240 ± 4</td>
<td>264</td>
</tr>
<tr>
<td>ι₆(f₂u), n.a.</td>
<td>-</td>
<td>96</td>
</tr>
</tbody>
</table>

*a* Determined in MgCl₂(aq) and Mg(ClO₄)₂(aq), see text.

*b* Unscaled HF/6-31G(d) wavenumbers of MgO₆ unit of the octadecaqua magnesium(II) (T₁₉ symmetry); taken from Pye and Rudolph ref. 20.
Captions for Figures

1) Raman spectrum (R$_{iso}$ format) of a 2.213 mol/kg Mg(ClO$_4$)$_2$ solution at 23 °C, showing the sum, component and (bottom trace) residual curves. The $v_1$-MgO$_6$ mode of Mg(OH)$_2$$_{6}^{2+}$ is at 358 cm$^{-1}$ and the broad OH…OClO$_3$ restricted translation mode is at ~235 cm$^{-1}$.

2) Raman spectrum (R format) of 2.742 mol/kg (NH$_4$)$_2$SO$_4$(aq) at 23 °C. A (50 to 700 cm$^{-1}$): $v_2$ and $v_4$ bending modes of SO$_4^{2-}$ at 452 cm$^{-1}$ and 617 cm$^{-1}$; OH…OSO$_3^{2-}$ restricted translation mode at ~190 cm$^{-1}$. B (920 to 1040 cm$^{-1}$): $v_1$-SO$_4^{2-}$ mode (note R$_{iso}$ $\approx$ R$_{pol}$ for this totally polarized mode). The broad, weak $v_3$-SO$_4^{2-}$ mode at 1110 cm$^{-1}$ [22] is omitted for clarity.

3) Concentration dependence of the $v_1$-SO$_4^{2-}$ Raman mode (R$_{iso}$ format) of (NH$_4$)$_2$SO$_4$(aq) at 23 °C. Inset: spectrum of 0.233 mol/kg (NH$_4$)$_2$SO$_4$ showing the detection of the isotopomer S$^{18}$O$^{16}$O$_3^{2-}$ at 964 cm$^{-1}$.

4) Concentration effects at 23 °C on the $v_1$-SO$_4^{2-}$ mode at ~980 cm$^{-1}$ in (NH$_4$)$_2$SO$_4$ solutions (filled circles) and in MgSO$_4$ solutions (after subtraction of the 993 cm$^{-1}$ component, open circles); A: peak position ($v_{max}$); B: fwhh.

5) Raman spectra (R$_{pol}$ format) of (NH$_4$)$_2$SO$_4$(aq) at 23 °C and MgSO$_4$(aq) at 23 and 120 °C at low wavenumbers, showing the restricted OH…OSO$_3^{2-}$ translation mode at ~190 cm$^{-1}$, the Mg$^{2+}$–OSO$_3^{2-}$ mode at ~245 cm$^{-1}$, the MgO$_6$ stretching modes at ~328 and 358 cm$^{-1}$, and the SO$_4^{2-}$ deformation modes, $v_2$ and $v_4$ at ~452 and 617 cm$^{-1}$.

6) Temperature effects on the R$_{iso}$ spectrum at low frequencies of 3.013 mol/kg MgSO$_4$(aq), showing the sum curve and component modes at A: 23 °C; B: 120 °C. Note the increasing importance at 120 °C of the 326 cm$^{-1}$ component of the $v_1$-MgO$_6$ mode and of the Mg$^{2+}$–OSO$_3^{2-}$ mode at 245 cm$^{-1}$.

7) Concentration dependence of the R$_{iso}$ spectrum in the $v_1$-SO$_4^{2-}$ region for MgSO$_4$(aq) at 23 °C.

8) R$_{iso}$ spectrum, showing the sum, component and (bottom trace) residual curves at 23 °C for A: 2.093 mol/kg MgSO$_4$ in H$_2$O; B: 2.106 mol/kg MgSO$_4$ in D$_2$O. Note that the isotopomeric component is included in the fit but omitted for clarity.

9) Correlation between the normalized integrated band intensities $I_{328}$/$(I_{328} + I_{358})$ and $I_{993}$/$(I_{993} + I_{980})$ for four concentrations (2.848; 2.106; 1.365, and 0.681 mol/kg) of MgSO$_4$(aq) at 23 °C.
10) Effects of temperature on the $v_1$-SO$_4^{2-}$ mode ($R_{iso}$ format) of 0.571 mol/kg MgSO$_4$(aq).

11) Fraction of sulfate species present as contact ion pairs as a function of [MgSO$_4$]$_T$, as determined by: Raman spectroscopy (present work, 23 °C, squares) and DRS (ref. 12, 25 °C, circles).

12) Comparison of the % species detected by Raman spectroscopy (upper panel) and by DRS (lower panel): filled triangles, 2SIP + SO$_4^{2-}$(aq); filled squares, SIP; filled stars, CIP + TI.

13) $R_{iso}$ spectrum for a solution containing 4.098 mol/kg MgCl$_2$ + 0.107 mol/kg MgSO$_4$ at 23 °C, showing the sum, component and (bottom trace) residual curves. For clarity, only a single component was used to fit the ‘free’ SO$_4^{2-}$ and the isotopomeric component (included in the fit) was omitted from the diagram. Note the appearance of the new mode at 1005 cm$^{-1}$, which has been assigned to a triple ion, Mg$_2$SO$_4^{2+}$(aq).
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10
Figure 11
Figure 12
Figure 13
Note added at proof: A recent Raman spectroscopic study by Tomišic and Simeon\textsuperscript{42} of nominally strong electrolyte solutions, including MgSO\textsubscript{4}(aq), has come to our attention since submission of this paper. No profiles for the $\nu_1$-SO\textsubscript{4}\textsuperscript{2-} mode were given\textsuperscript{42} but the component peak positions derived by evolving factor analysis (EFA) were stated to be 984 cm$^{-1}$ for ‘free’ sulfate and 989 cm$^{-1}$ for the CIP. These differ markedly from the present results and those of others.\textsuperscript{7,10} Although insufficient detail (such as scattering geometry, spectral resolution, etc.) was presented to allow a proper assessment of the spectra of Tomišic and Simeon,\textsuperscript{42} the stated sampling interval of 2 cm$^{-1}$ is probably too large for precise profile analysis by EFA or other common curve fitting techniques. With such smeared-out profiles it is not surprising that their peak locations differ from, and that they were unable to detect the effects observed in, the present study. The suggestion by the authors\textsuperscript{42} that EFA had not been used previously in Raman spectral studies of ion association appears to have overlooked the 1977 review by Shurvell and Bulmer.\textsuperscript{43}
