Comment on “Dynamic ion association in aqueous solutions of sulfate”

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Recently in this journal, Watanabe and Hamaguchi1 (WH) suggested that the Raman spectra of aqueous solutions of MgSO$_4$ at ambient temperatures can only be explained in terms of their “dynamic exchange model” rather than what they describe as “the conventional static equilibrium model.” The latter is actually Eigen’s dynamic three-step ion-pairing model of ion association,3–6 designated as “static” on the Raman time scale by WH in that it implies separate observables $v_1(a_1)$ vibrational modes for “free” $\mathrm{SO}_4^{2−}$(aq) ions (at $\sim982$ cm$^{-1}$) and for the bound sulfate (at $\sim993$ cm$^{-1}$ in MgSO$_4$ solutions).6 The latter mode, by common consensus, corresponds only to the presence of contact ion pairs (CIPs, or inner sphere complexes): the last species formed in the Eigen model.5,6

The model of WH was proposed on the basis of their coherent anti-Stokes Raman spectroscopic (CARS) measurements of MgSO$_4$(aq) and related solutions,1,8 which failed to detect the separate modes of differing depolarization ratio ($\rho$) that would be expected for an equilibrium mixture of free ($\rho=0$) and bound ($\rho \neq 0$) sulfate. Instead, it was claimed by WH that the $v_1(a_1)$ band corresponds only to a single mode “broadened homogeneously with a finite depolarization ratio.”

Although the observations of WH are at least partly correct, their interpretation (which ignores most of the large body of existing Raman, thermodynamic, and relaxation data) is not. For convenience and brevity the comments below are restricted to MgSO$_4$(aq) solutions but similar arguments can be applied to the other sulfate systems studied by WH.

Consistent with the CARS observations of WH,1 our Raman measurements on MgSO$_4$(aq), Fig. 1, confirm that the $v_1(a_1)$ mode of free $\mathrm{SO}_4^{2−}$ at $\sim982$ cm$^{-1}$ possesses a very small depolarization ratio of 0.0035±0.0010.6,9 However, the same value of $\rho$ is observed in $(\text{NH}_4)_2\mathrm{SO}_4$(aq) solutions10 which are generally considered to be fully dissociated. This suggests that the very small but finite depolarization of this mode arises from a slight departure of the free hydrated sulfate ion from ideal $T_d$ symmetry, consistent with theoretical calculations.9,10 Furthermore, in the anisotropic Raman spectrum of MgSO$_4$(aq) a weak contribution at 993 cm$^{-1}$ with $\rho=0.006\pm0.002$ has also been observed,8 although it is difficult to quantify at room temperature (cf. Fig. 1) because CIPs are only a small percentage of the overall sulfate concentration.5,6 At higher temperatures, where the CIP content rises, this mode increases markedly (Fig. 2; see also Fig. 5 of Ref. 9). Similar results are obtained when the CIP concentration is increased by adding a large excess of MgCl$_2$ to SO$_4^{2−}$ (Fig. 11 of Ref. 5 and Fig. 13 of Ref. 6) or by using supersaturated solutions.11,12

As recognized by WH (Ref. 1, p. 034508), the dramatic increase in CIP concentrations with increasing temperature (Fig. 2) contradicts their model, which would predict that $v_1(a_1)$ should broaden dramatically and coalesce into one mode. However, there is no doubt that CIPs are detected and that their concentration increases with increasing temperature since both effects are quantitatively confirmed by relaxation measurements (see below).

It should also be noted that solutions of MgSO$_4$ in D$_2$O show almost identical features: $\rho=0.004\pm0.001$ (Fig. 2; see also Fig. 3) for free sulfate at $\sim982$ cm$^{-1}$ and $\rho=0.006\pm0.002$ for the CIP at $\sim993$ cm$^{-1}$ (Fig. 3). This argues strongly against the perturbation of the $v_1(a_1)$ mode being due to solvent effects or “dynamic exchange.”

![Fig. 1. Raman spectra, $I_{\text{pol}}$ (upper curve) and $100I_{\text{depol}}$ (lower curve), of a 3.013 mol/kg MgSO$_4$ solution in H$_2$O at 22 °C (Ref. 9).](image-url)
We now briefly consider some of the other extensive evidence available on the nature of MgSO₄ solutions, which has largely been ignored by WH. We emphasize that similar (although less comprehensive) evidence exists for many other sulfate systems.

First, there is a 1:1 correspondence between the Raman intensities of the relevant \( \nu_1(\text{Mg–O}) \) and \( \nu_1(\text{S–O}) \) modes (at 328 and 993 cm\(^{-1} \), respectively), exactly as is required for the formation of a MgSO₄ CIP (see Fig. 9 of Ref. 6 and accompanying text).

Second, the detection of CIPs by Raman spectroscopy is not unique. Almost identical results are obtained by dielectric relaxation spectroscopy (DRS), which being sensitive to dipole moment is able to detect and distinguish all three ion-pair types (double solvent separated, 2SIP, and solvent shared, SIP, as well as CIPs), see particularly Fig. 11 of Ref. 6. Furthermore, DRS data also show a similar increase of the concentration of CIPs with increasing temperature (Fig. 4).\(^{13} \)

Third, DRS (which detects species) and ultrasonic relaxation (USR, which detects equilibria) studies of MgSO₄(aq) are in quantitative agreement with respect to the number of ion-pair types and their formation constants (see particularly Fig. 7 of Ref. 5).

Fourth, the association of MgSO₄, as presented by WH (their Scheme 2), yields an overall association constant of \( K = W_1 / W_2 \approx 250 \text{ fs}/10 \text{ ps} \).\(^{14} \) This is four orders of magnitude less than the values obtained from the numerous thermodynamic, conductivity, and relaxation studies, all of which are in good agreement with each other.\(^{15} \)

Fifth, the rate of dissociation of the CIP proposed by WH (\( W_2 = 4 \times 10^{12} \text{ s}^{-1} \)) is more than four orders of magnitude greater than the diffusion-controlled rate constant predicted by the Eigen model for the decay of CIPs (\( \sim 1.6 \times 10^8 \text{ s}^{-1} \) (Ref. 16) and approximately seven orders of magnitude greater than actually observed by Eigen and Tamm\(^{3,4} \) \( 8 \times 10^5 \text{ s}^{-1} \) and confirmed by Atkinson and Petrucci\(^{17} \), both using USR. In addition, for an ion pair to be detected by DRS its lifetime has to be at least approximately the same as its rotational correlation time \( \tau_\text{rot} \) (roughly 2/3 of its dielectric relaxation time). For CIPs in MgSO₄(aq) the experimental relaxation time\(^{5} \) gives \( \tau_\text{rot} \approx 15 \text{ ps} \), consistent with the Stokes-Einstein-Debye equation. This \( \tau_\text{rot} \) value is 60 times larger than the ion-pair lifetime claimed by WH. If WH were right, CIPs would not be detected by DRS, whereas objectively (Fig. 4) they are.

There are many other criticisms that can be made of WH’s arguments but these are unnecessary here. It is clear that their dynamic exchange model cannot explain the large body of Raman, relaxation (both DRS and USR), and thermodynamic data that exists for the MgSO₄(aq) system either
at ambient or elevated temperatures. On the other hand, all of these data can be readily accounted for by the presence of multiple equilibria involving different types of ion pair: the Eigen model. Similar considerations apply to other sulfate systems studied by WH. The very small depolarization ratios of the $\nu_1(a_1)$ mode for $\text{SO}_4^{2-}$ reported by WH and confirmed by us (Fig. 1) (Refs. 9 and 10) can be explained by a slight decrease in its symmetry upon hydration. Indeed, such an effect has been invoked in an infrared study of sulfate in water to explain the observation of a weak band at 982 cm$^{-1}$, assigned to the $\nu_1(a_1)$ mode for $\text{SO}_4^{2-}$, which is forbidden in the IR for a fully symmetric $T_d$ species.

$\text{SO}_4^{2-}$

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2. WH do not actually specify the temperature of their measurements but ambient conditions can be inferred.


7. Solvent-separated ion pairs (2SIPs and SIPs) do not usually cause sufficient perturbation to be detected via the anionic vibrational modes; very occasionally SIPs (outer-sphere or bridged complexes) have been reported (see Ref. 6 and references cited therein).


12. Other changes also occur both upon addition of MgCl$_2$ (Refs. 5 and 6) and in supersaturated solutions (Ref. 11) but these do not alter the thrust of the argument.


14. Note that the numbers referred to as the ‘lifetimes’ of the free (10 ps) and bound (250 fs) states in Scheme 2 of WH (Ref. 1) are reciprocal rate constants. Strictly, according to Schemes 1 and 2, the forward reaction is second order. This means that $W_{1/c_+}$ (or $W_{1/c_-}$; both = $W_1/c$ for the small association constant) is the true forward rate constant and therefore $K = \text{forward rate}/\text{backward rate} = 0.063$ at 1M. This does not change the argument significantly as this value is still many orders of magnitude lower than the thermodynamic and relaxation results.


