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Ab initio molecular dynamics simulations of speciation of $MgSO_4$ solution at 543K

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The migration of sulfate-bearing brines is in direct relevant to metal sulfide deposits formation. Liquid-liquid phase separation has been found in $MgSO_4$-H_2O system over 533 K, promoting the enrichment and transportation efficiency of sulfate.[1, 2] A new component in rich concentration liquid phase has been revealed by Raman spectroscopy with a peak at ~1020 cm^{-1} and it was interpreted as chain structure polymers.[1, 2]

We performed *ab initio* molecular dynamic simulations to disclose the speciation of rich $MgSO_4$ droplet by using CP2K/QUICKSTEP package with Perdew-Burke-Ernzerhof (PBE) functional and PBE0 functional at 543 K and 330 K in NVT ensembles. The trajectories were then analysed by TRAVIS to acquire vibration frequencies from autocorrelation functions of velocities, dipole moments and polarizabilities.

Our results show that the components generating ~ 1020 cm^{-1} should be interpreted as dehydrated cluster with S-4M (SO_4^{2-} surrounded by 4 Mg^{2+}) association. The similarity between S-4M structure in rich liquid phase and kieserite ($MgSO_4 \cdot H_2O$) implies the nucleation pathway of spinodal decomposition. Furthermore, the cause for *v*-980 (symmetric stretching mode of SO_4^{2-}) shifting in Raman spectra has been disclosed and attributed to the chemical surroundings of SO_4 tetrahedra. Wavenumber ~990 cm^{-1} represents the existence of 1 monodentate Mg-Os bond, ~1000 cm^{-1} reflects the association with at least 2 Mg^{2+}, and ~1005, 1020 cm^{-1} is related to 3 or 4 Mg-Os bonding, respectively. So, the split Raman peaks represents more monodentate Mg-Os associations, and more complex components may form. In addition, the free energy calculations reveal the stability of monodentate contact ion pair (CIP, Mg^{2+}-SO_4^{2-} pair) compared to bidentate CIP in homogenous solution at 543 K. However, the *v*-980 mode of bidentate CIP shows ~10 cm^{-1} decrease, which makes the experimental Raman spectrum analysis to be more intricate for systems prefer bidentate associations.

Our findings give accurate atomic level recognition of concentrated phase in liquid-liquid phase separation and theoretical explanation of the *v*-980 Raman peak shifting, which inspire on nucleation processes of hydrated $MgSO_4$ minerals and Raman spectra resolving of other sulfate systems.

[1]Wang *et al.* (2013) Geochimica et Cosmochimica Acta **103**, 1-10. [2]Wan *et al.* (2015) The Journal of Physical Chemistry A **119**, 9027–9036.