

Research Article

Ab Initio Molecular Dynamics Simulations and Vibrational Frequency Calculations of Species in Liquid-Liquid Phase Separated MgSO₄ Solution at 543K

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The transport of sulfate-bearing brines is closely relevant to mineralization of sulfide deposits as metal-sulfate complexes exist in hydrothermal fluids. Liquid-liquid phase separation evidently occurs in various metal-sulfate systems with transport and precipitating different from homogeneous fluids. Previous studies have revealed a new species with a Raman peak at ~1020 cm⁻¹ in rich concentration phase of liquid-liquid phase separated MgSO₄ solution, and it was interpreted as chain structure polymers. *Ab initio* molecular dynamics simulations (AIMD) and autocorrelation functions for frequency calculation have been performed to disclose the speciation. The results show that more Mg²⁺ ions surrounding a SO₄²⁻ anion lead to higher wavenumber of Raman peaks, which indicates the formation of complicate clusters with ion associations similar to kieserite. Besides, the splitting peaks of *v*-980 Raman bands at ~980, 990, and 1005 cm⁻¹ in homogeneous solution represent more monodentate Mg-Os (Os: O of SO₄²⁻) associations instead of certain species, which favors the formation of prenucleation. Our findings give atomic level recognition of concentrated phase in liquid-liquid phase separated MgSO₄ fluids and theoretical explanation of the 980 cm⁻¹ Raman peak shifting, which will further inspire understandings on nucleation processes of hydrated sulfate minerals and Raman spectra resolving of other sulfate systems.

1. Introduction

 Mg^{2+} and SO_4^{2-} are the most abundant ions except for Na⁺ and Cl⁻ in seawater [1], and SO_4^{2-} is commonly abundant in natural fluid inclusions captured in diagenetic and hydrothermal minerals [2], which directly reflects the evolution of fluids in the earth crust. Sulfate-bearing brines have also been widely sampled in sedimentary basins [3, 4] and hydrothermal vents on the seafloor [5]. The transport and chemical evolution of fluids in these systems play crucial roles in mineralization of metals [6]. For instance, during mineralization of many epithermal-mesothermal metal sulfide deposits, sulfate ions in hydrothermal fluid originated from deep crust had been reduced into HS^- or S_n^{2-} and induced precipitating of metal sulfides [7–9]. In addition, hydrated MgSO₄ minerals have been found on extraterrestrial planets [10, 11], and further measurements indicate that Mg²⁺ and SO₄²⁻ are dominant dissolved ions in shallow subsurface [12].

Physical chemistry of aqueous $MgSO_4$ solutions at low temperatures has been studied extensively. Analysis of its dielectric relaxation spectra indicates the existence of different associated species: double solvent separated ion pair (2SIP), solvent separated ion pair (SIP), and contact ion pair (CIP) [13]. Triple ions (TI) are also suggested for more concentrated solution (>1.0 M) [13, 14]. Furthermore, Raman spectra have been introduced to build a link between the shifting of the symmetric stretching mode of sulfate (v-980) and these associated species. Most studies agree that the shifting is caused by the formation and increasing concentration of more associated species [15-17]. So, the split peaks at ~980, 995, and 1005 cm⁻¹ are usually assigned to unassociated SO₄²⁻ (e.g., free sulfate anion, 2SIP, and SIP), CIP, and TI or larger complexes, respectively [15-17]. Recent studies have observed liquid-liquid phase separation of binary MgSO₄-H₂O system over 533 K at vaporsaturation pressures [16, 18], which likely promotes enrichment and transport efficiency of sulfate [19]. The formation of rich concentration liquid droplets is suspected to resemble a prenucleation process [20]. The in situ measured Raman peak around 1020 cm⁻¹ of the concentrated liquid phase has been explained as a possible emergence of chain structure polymers [16, 18]. However, the experimental perspectives of the speciation of liquid phase have not been well established. Although molecular simulations have provided a microscopic information of MgSO₄ solution [21-24], the specialty of liquid-liquid phase separation at high temperatures has not been considered yet. The species corresponding to the peaks at ~1020 cm⁻¹ in the concentrated phase differ from those in homogeneous solutions. Whether it represents chain structure polymers remains questionable. Moreover, the preference of monodentate or bidentate association between Mg^{2+} and SO_4^{2-} is also unknown. A better understanding of these questions could potentially shape our knowledge about the liquid-liquid separated phases and its relationship with prenucleation processes.

Once the fluid speciation is recognized, the corresponding vibration frequencies can be computed to further invert to the measured Raman spectrum data, which can theoretically explain the shifting of v-980 mode. Vibration properties are traditionally derived from static calculations, in which the frequencies are given by the diagonalized Hessian matrix at the minimum of potential energy surface. In this method, the solvent effects are usually considered by adding a hydrated shell and a solvation model is used to account for the dielectric effect [25]. The vibrational frequencies of CIP, TI, or chain structure from static calculations for MgSO₄ solution have been discussed, which supports the interpretation of experimental measurements [22, 24]. However, the geometry optimization and averaging over the phase diagram become the major obstacles in this approach. In the last decade, ab initio molecular dynamics (AIMD) simulations have been used to derive vibrational frequencies [26], where different configurations of liquid phase space can be easily sampled and the solvent influence such as hydrogen bond interaction is considered naturally [27, 28]. The AIMD based on spectroscopy techniques has been applied to investigate the speciation of MgSO₄ fluids at high temperatures and pressures, and the results suggested that individual species cannot be resolved by Raman spectra [21].

In this study, we performed AIMD simulations of $MgSO_4$ solution at 543 K to acquire the ion-ion associations of SIP, CIP, and TI, and the free energy changes between those species. The vibrational frequencies were further computed form AIMD trajectories to theoretically explain *v*-980

mode shifting. The relationship between methods is expressed as a flowchart in Figure S1. The speciation of rich-phase is investigated in detail, and the results differ from previous interpretations.

2. Methodology

2.1. Models and Computational Details. To construct the models, sulfate anions and the complexes of $MgSO_4$ were placed inside aqueous systems (Table 1). The structures of $SO_4^{2^-}-Mg^{2^+}$, $SO_4^{2^-}-Mg^{2^+}-SO_4^{2^-}-Mg^{2^+}$ and more complicate structures of $SO_4^{2^-}-3Mg^{2^+}$, $SO_4^{2^-}-4Mg^{2^+}$, and $4SO_4^{2^-}-4Mg^{2^+}$ are shown in Figure 1 and denoted as CIP, S-M-S, M-S-M, S-3M, S-4M, and 4S-4M, respectively. The number of water molecules for the corresponding system was derived from the equation of the state of water at a certain temperature and corresponding saturated vapor pressure [29]. The concentration of $MgSO_4$ in CIP ensemble is 0.66 M.

All AIMD simulations were performed by using CP2K/ QUICKSTEP package implemented with Gaussian and plane wave (GPW) scheme for density functional calculation [30, 31]. The Perdew-Burke-Ernzerhof (PBE) functional [32] and PBE0 ($\alpha = 0.25$) hybrid functional [33, 34] both combined with DFT-D3 dispersion correction were employed to account for the exchange-correlation energy [35]. Goedecker-Teter-Hutter (GTH) pseudopotentials were applied to represent the core electrons [36]. For PBE functional, double- ζ valence polarized (DZVP) basis sets [37] were used for H, O, S, and Mg. Specifically, basis sets with 2 (q2) and 10 (q10) valence electrons were employed for Mg with the corresponding cutoff in the reciprocal space to be 300 Ry and 800 Ry, respectively. Most calculations were carried out under Mg-q2 criteria for computational efficiency. PBE functional was used for all free energy calculations. For PBE0 functional, the Hartree-Fock exchange energy was obtained using the auxiliary density matrix method (ADMM) [38] with cFIT3 auxiliary basis set. PBE0 was additionally introduced particularly for calculating vibrational property because of its accuracy compared to the results from PBE. The discussion of PBE and PBE0 could be found in the Section 5 of Supporting Information (SI) (Figure S4, Figure S5, and Table S3).

Born–Oppenheimer molecular dynamics simulations were performed in NVT ensembles with a time step of 0.5 fs. The temperature was controlled using the Nosé-Hoover thermostat [39] at 330 K and 543 K. 543 K was chosen in accord with the condition when phase separation happens. 330 K was chosen to enhance the ergodicity of the ensemble at ambient conditions [40].

2.2. Free Energy Calculation. A series of constrained AIMD simulations were executed to derive the free energy profile of Process (1)-(3) at 543 K.

$$CIP \longrightarrow SIP$$
 (1)

 $S - M - S \longrightarrow CIP + SO_4^{2-}$ (2)

$$M - S - M \longrightarrow CIP + Mg^{2+}$$
 (3)

TABLE 1: Components and size of the simulated models.

T (K)	Anions and ions	Number of water	Length of the cube (Å)
543	SO4 ²⁻	61	13.56
	CIP	61	13.56
	S-M-S	122	17.09
	M-S-M	122	17.09
330	SO4 ²⁻	61	12.48
	CIP	61	12.48
	S-M-S	122	15.73
	M-S-M	122	15.73
	S-3M	120	15.73
	S-4M	120	15.73
	4S-4M	110	15.73

The distance between Mg and S was chosen as the reaction coordinate (r). The potential of mean force (PMF), ΔF , was obtained by integrating the mean force (f) along r, according to the following formula [41]:

$$\Delta F(r) = -\int_{r_0}^r f(r') dr'.$$
(4)

Process (1) was first calculated to find the reaction coordinate r_1 of the most stable point. Then, by fixing one Mg-S distance of S-M-S or M-S-M at r_1 while changing the length of the other Mg-S distance, the free energy curves of process (2) and (3) were obtained.

2.3. Vibration Calculation. TRAVIS [27, 42] was used for computing the vibrational spectra directly from AIMD trajectories. The spectra were deduced from the Fourier transform of autocorrelation functions of certain variables from trajectories: power spectra are derived from the particle velocities, IR spectra are obtained from molecular dipole moments, and Raman spectra rely on molecular polarizabilities. The detailed expression of autocorrelation functions is defined in SI Section 1.

The production time of ensembles at 330 or 543 K was above 15 ps for frequency analyzing after a prior equilibration AIMD run for at least 2.5 ps. The dipole moment was acquired from Wannier centers localized at every fifth time step of the trajectory. An external electronic field with the strength of 2.57×10^8 Vm⁻¹ was employed to obtain polarizability, and the laser wavelength for computing Raman intensity was set to be 532 nm.

2.4. Hydrogen Bond Recognition and Lifetime Calculation. In order to analyze the chemical surrounding of sulfate anion and its influence on the *v*-980 mode, the criterion of hydrogen bond (HB) is defined drawing on the experience of Xenides et al. [43] and Kumar et al. [44]. To suit our systems, the range of hydrogen bond distance $d_{O...H}$ was set to be $1.2 \le d_{O...H} \le 2.3$ Å, and the angle $\theta_{O-H...O}$ to be $\ge 130^{\circ}$. The distribution diagram of $d_{O...H}$ and θ can be found in Figure S2.

The following time autocorrelation function [45] is employed to measure the lifetime of hydrogen bonds:

$$C_{x}(t) = < \frac{\sum h_{ij}(t_{0})h_{ij}(t_{0}+t)}{\sum h_{ij}(t_{0})^{2}} > , \qquad (5)$$

where $h_{ij}(t)$ is a binary measure of whether a pairing *ij* meets the geometric criteria at time t ($h_{ij} = 1$ or $h_{ij} = 0$). A range of t_0 was picked to average over under the interval of 0.01 ps, and at least 10000 time steps were counted for each t_0 . The relevant lifetime τ_x is defined as

$$\tau_x = \int_0^\infty (C_x(t) - C_x(t = \infty))dt.$$
(6)

The integration was handled in two ways. One is doing a trapezoidal integration directly. The other is matching the points into the following target function, according to Gowers and Carbone [46]:

$$C(t) = A_1 e^{-k_1 t} + (1 - A_1) e^{-k_2 t}.$$
(7)

Detail process and fitting parameters of A_1 , k_1 , and k_2 are listed in Table S1 of SI.

3. Results

3.1. Free Energy Profiles at 543 K

3.1.1. $CIP \rightarrow SIP$. There are three pits on the free energy curve of the transition from CIP to SIP structures (Figure 2(a)), corresponding to bidentate complex at 2.8 Å, monodentate complex at 3.3 Å, and SIP at 4.9 Å, respectively. Starting at 2.8 Å, the free energy goes up by 2.41 kcal/mol to reach the first peak at 3.0 Å and then drops to the second pit of the monodentate complex. The free energy difference between bidentate and monodentate structure is 1.21 kcal/mol, which means that they can transform easily due to a low energy barrier of 2.41 kcal/mol. The difference in free energy between the monodentate complex and SIP is 4.04 kcal/mol, but the energy barrier is as high as 7.38 kcal/mol, i.e., the second peak at 4.0 Å with the free energy rising by 7.38 kcal/mol from the minimum point at 3.3 Å. So, the structure of CIP dominates in solution and tridentate complex seems not possible to form.

3.1.2. $S-M-S \rightarrow CIP + SO_4^{2^2}$. Similar phenomenon can be found in the S-M-S system. The global minimum point at the free energy curve corresponds to the monodentate structure at 3.3 Å (Figure 2(b)). There is a small energy barrier of 1.89 kcal/mol between the bidentate structure at 2.8 Å and the monodentate structure at 3.3 Å, and the difference in free energy between these two structures is only 0.9 kcal/mol. Transforming from the monodentate structure (at 3.3 Å) to sulfate anion (at 4.8 Å), a peak of 5.82 kcal/mol should be overcome. The free energy difference between monodentate complex and dissociated structure is only 1.76 kcal/mol, which is much lower compared to 4.04 kcal/mol for Process (1), implying that longer chains are harder to form.



FIGURE 1: Hydration structures of complexes in water in equilibrium. Color key: O = red; H = white; Mg = pink; S = yellow. Not all water molecules are displayed here.



FIGURE 2: The PMF for processes (1)-(3). The error bar is the integral of errors at every *r* of the mean force. Details for calculating errors can be found in SI Section 4 and Figure S3. The snapshot of Bi-S-M-S and Bi-M-S-M can be found in Figure S7.

3.1.3. M-S-M \rightarrow CIP + Mg^{2+} . The shape of PMF curve for Process (3) shown in Figure 2(c) is similar to the other two. The free energy differences between bidentate and monodentate structures and monodentate and dissociated structure are 1.82 and 1.33 kcal/mol, respectively. The energy barrier between a monodentate and dissociated structure is 5.73 kcal/mol, while that between bidentate and monodentate structures is only 2.2 kcal/mol. The mean force for every r of those three processes is displayed in Figure S3. It is noted that in Process (2) and (3), a premise of Mg-S distance at one side to be 3.3 Å has been artificially set, which assumes that the minimum free energy point of TIs would vary along the line where one side distance is 3.3 Å. The system's degree of freedom is decreased. However, based on the data of Process (1) where Mono-CIP is the most stable structure, the deviation would be tolerable.

3.1.4. Estimation of Association Constant. On the assumption that PMF represents the infinite dilute condition [47], the ion-pair association constant K_A can be derived from the equation

$$\begin{split} K_{\rm A} &= N_{\rm A} 10^{-27} \int_0^{r_{\rm c}} 4\pi exp\left(\frac{-\Delta F(r) + W(r_0)}{kT}\right) r^2 dr, \\ W(r_0) &= \frac{-q^2}{4\pi \varepsilon r_0 \varepsilon_0}, \end{split} \tag{8}$$

where $r_{\rm c}$ is the cutoff distance distinguishing free ions and associated ion pair, $N_{\rm A}$ is the Avogadro constant, k is the Boltzmann constant, and ε_0 is the vacuum permittivity. Here, $r_{\rm c} = 4.0$ Å and $r_0 = 6.0$ Å were chosen according to the PMF of CIP \rightarrow SIP. The relative permittivity ε of pure water under 542 K is 24.38 [48], and the water density is 0.767 g/cm³ [29]. The value of log K_A is 6.2 kg mol⁻¹ (K_A (L mol⁻¹) is converted into the molarity-based association constant $K_A(m)$ (kg mol ¹) by multiplying the water density ρ (g/cm³)), which, in other words, represents the occupation of almost 100% CIPs under the condition that only CIP and SIP exist in the solution. It is worthy to note that states of 2SIP and 3SIP cannot be calculated because of the limitation of system size, which contradicts the premise of infinite dilute condition and cause overestimation of K_A . Furthermore, the spherical integral of the formula hypothesizes that the ion pairs of CIP, SIP, 2SIP, etc., can go through the r-radius spherical surface ergodically. It is credible for simple ion pairs such as Na⁺-Cl⁻ but not for $Mg^{2+}-SO_4^{2-}$ pairs, because of the symmetry of SO_4 tetrahedra, which ultimately also contributes to the overestimation of K_A . Nevertheless, dielectric relaxation spectroscopy for MgSO₄ solution at 338 K suggests that the fractions of 2SIPs and SIPs strongly reduce with temperature (log K_A changes from 2.2 to ~5 kg mol⁻¹ as T changes from 278 K to 338 K) [14]. Furthermore, the mole ratio of monodentate CIP and bidentate CIP can be roughly estimated by

$$\frac{\text{Mole}_{\text{Bi-CIP}}}{\text{Mole}_{\text{Mono-CIP}}} = e^{-\Delta A/kT},$$
(9)

where ΔA is the free energy difference between monodentate CIP and bidentate CIP which equals 1.21 kcal/mol. The value of this ratio is 0.32, which means that ~24% CIPs are bidentate.

3.2. Vibration Frequency

3.2.1. Analysis of Free Sulfate Anion, CIP, and TI. We performed a series of calculations to bridge Raman spectra to aqueous speciation. For the reason that CIPs and TIs could exist in homogenous solutions from the PMF curves, these components were first tested (Table 2 and Figures 3(a)– 3(c) and 4(a)–4(c)). Computational frequencies of free $SO_4^{2^-}$ and monodentate CIP at 330 K are in good agreements with the experimental data, while the wavenumber of bidentate CIP behaves oppositely by decreasing to 966 cm⁻¹. As temperature goes up, the descending tendency of all frequencies is also in consistent with experimental observations. However, the frequencies of TIs do not significantly ascend, disaccord with the experiment interpretation of peaks at ~1005 cm⁻¹ [15–17].

The intrinsic cause for the shifting of sulfate anion's v-980 mode results from its chemical surroundings: bonding with Mg²⁺ and water molecules. Under 330 K, SO₄²⁻ of Mono-CIP possess 7.4 HBs (Table 3), while free sulfate anion obtains 9.0 HBs. M-S-M gains 2 Mg-Os bonds and 5.7 HBs around SO₄²⁻. From the fact that the frequencies of M-S-M and Mono-CIP are higher than free sulfate anion, monodentate Mg-Os bond shows a greater influence than HB (Table 3). However, the bidentate connection acts oppositely because *v*-980 mode is symmetrical stretching and bidentate interaction would cause unevenly weighing from one side. Moreover, the HB number decreased as temperature goes up, implying weakened bond interaction, which leads to the decrease of *v*-980 mode.

3.2.2. Analysis of S-3M, S-4M, and 4S-4M. Given that Mg-Os plays an important part for blue shift of v-980 mode, models (S-3M, S-4M, and 4S-4M) containing more Mg-Os interactions were designed. S-3M shows the frequency of 1004 cm⁻¹, while the data for S-4M is 1022 cm⁻¹, which strongly supports our conjecture (Table 2 and Figures 3(d) and 4(d)). As more Mg-Os bonds form around SO_4^{2-} , a higher wavenumber of v-980 mode would appear, which indicates complex clusters with S-3M and S-4M associations correspond to the signals at 1005~1020 cm⁻¹. In Figure 3(c) and Figure S4(d) in SI, the calculated Raman spectra of S-4M and Bi-CIP are in poor performance compared to other calculated species, which is probably due to the errors caused by the localization of Wannier centers and the limited orientation of sulfate anions.

The former ensembles of S-M-S, M-S-M, S-3M, and S-4M are not charge neutral, which causes an artificial inaccuracy on the total energy. Frequency calculation of charge unbalanced TI structures was performed in former study [24], and its influence is negligible. A charge neutral cluster

of 4S-4M was simulated under PBE0/330 K (Table 4) in contrast to charge unbalanced systems. Four sulfate anions were analyzed separately. Both S2 and S3 share a similar chemical surrounding with 2 Mono-CIP association, similar to ~10 cm⁻¹ increase of M-S-M. For S1, because of the existence of bidentate association, no obvious rise has been observed. As for S4, although 2 monodentate Mg-Os bonds exist, only an average of 4.1 HBs were gained, compared to 5.7 HBs in M-S-M, which neutralized the effect of Mono-CIP association. In total, the result of 4S-4M cluster agrees well with our former conjecture given that only the number and types of bonds are considered here.

3.2.3. Results of Power Spectra and Infrared Spectra. The ideal model of SO_4^{2-} belongs to T_d molecule point group, and 2 vibrations are IR active in triple degeneracy. All frequencies are Raman active. However, with the influence of Mg ions, the symmetry of SO_4 tetrahedron degrades and the former degenerate mode would split (Figures 4 and 5 and Table 5). The splitting of V_4 mode in infrared spectra is obvious almost for all the associated species (Figure 5). The splitting of V_1 and V_2 in the power spectra of Bi-CIP indicates its D_{2d} symmetry [49] (Figure 4(c)). The splitting of V_4 in M-S-M, S-M-S, and Mono-CIP indicates its $C_{2\nu}$ or $C_{3\nu}$ symmetry caused by monodentate Mg-Os bond.

4. Discussion

4.1. Speciation in Homogeneous MgSO₄ Solution and Raman Spectrum Analysis. The PMFs give a picture of the stability of SIP, CIP, and TI species in homogenous MgSO₄ solution at 543 K. CIPs dominate in the homogenous solution, which accords with dielectric and Raman spectra [14-16]. The intriguing point is that bidentate CIP is less stable than monodentate CIP because of the high solvation energy of Mg^{2+} ion with its extremely stable hydration shell [51]. The formation energies of monodentate, bidentate, and tridentate MgSO₄ CIP previously calculated by using DFT show that bidentate and tridentate CIPs are stable with negative formation energies [23], but this viewpoint is in question because no water molecule was considered in the calculation. The effect on v-980 mode of monodentate is also different from bidentate CIP associations. Monodentate CIPs or chemical condition similar to CIPs (e.g., S-M-S) shows a ~10 cm⁻¹ blue shift, which agrees with most experiments [14-16, 21] and previous simulations [22, 24]. Bidentate CIP shows a 10 cm⁻¹ decrease, which was also reported by Zhang et al. [24]. The free energy calculations of CIPs to TIs reveal the formation of TIs in a relatively low percentage compared to CIPs. The peak at wavenumber $\sim 1005 \,\mathrm{cm}^{-1}$ represents TIs in high concentration homogeneous MgSO4 solution [15-17]. However, our data do not uniquely support the assignment of this peak to TIs (S-M-S, M-S-M) as they are both under 1000 cm⁻¹.

To clarify the speciation in homogeneous $MgSO_4$ solution and its relation with Raman spectra, it is crucial to reveal the cause of *v*-980 mode shifting. Former Raman spectroscopic studies [15, 17] have pointed out the difference between $MgSO_4$ and $(NH_4)_2SO_4$ solution. At ambient

TABLE 2: Vibration frequency of possible components.

<i>T</i> (K)	Free SO ₄ ²⁻	CIP		TI		6.214	C 414
		Mono-	Bi-	S-M-S	M-S-M	5-31VI 5-	5-4M
330	985*, 983	991*, 990	961*, 966	985*, 987	994*, 994	1004*, 1004	1022*
543	973*, 973	985*, 983	-	-	983*, 983	-	-
Exp. [16, 17, 21]	980	99	95	10	05		

The data is the peak value of the ν -980 mode. Numbers with * were deduced from autocorrelation functions of velocities, and others were deduced from autocorrelation functions of polarizabilities. "-" represents the corresponding unstable structures, and their accurate frequencies could not be counted.



FIGURE 3: Calculated Raman spectrum of sulfate anion for different complexes. The intensity is from isotropic polarizability.

temperature, the *v*-980 peak shifts to higher wavenumber and becomes increasingly asymmetric as the MgSO₄ concentration rises; however, it remains symmetric in $(NH_4)_2SO_4$ solution because NH_4^+ and SO_4^{2-} are thought to be fully dissociated. For strong electrolytic sulfate solution other than Mg^{2+} (e.g., Zn^{2+} and Cd^{2+}), same tendency of *v*-980 mode shifting has been found [19, 52–54]. Those similarities directly indicate the similar bonding condition surrounding SO_4 tetrahedra. Effects of HB interactions on vibrational frequencies of anions (e.g., PO_4^{3-} and SO_4^{2-}) have been discussed by static cluster calculations. As more surrounding water was added, the wavenumber of *v*-980 evidently increases [24, 55]. In this study, AIMD simulations of CIPs, TIs, S-3M, and S-4M confirm the contribution of Mg-Os bond interaction to the blue shift of v-980 mode. Wavenumber above 1005 cm⁻¹ mainly originates from SO₄ tetrahedra involving 3 or 4 Mg-Os bonds, while peak of 2 Mg-Os associations (e.g., M-S-M and 4S-4M) is around 994-1000 cm⁻¹. The static calculation of M-S-M cluster from Zhang et al. [24] corresponds to a peak of 1023 cm⁻¹ with a scaling factor of 0.9524; however, this factor could contribute artificial errors to the result. Jahn and Schmidt [21] calculated vibrational spectra for possible species in MgSO₄ solution at 1000 K by using AIMD simulations and found that the peak of S-M-S is weaker than that of Mg₂(SO₄)(MgOH)³⁺, which implies that more associated species have higher frequencies.



FIGURE 4: Power spectra of sulfate anion in different complexes.

TABLE 3: Analyzing of hydrogen bond for different species.

Models	T(K)	Numbe	Number of HB		
Widdels	1 (K)	s-w	W-W		
Eres sulfate anion	330	9.0	3.0		
File suitate amon	543	6.7	1.2		
Mono CIP	330	7.4	3.0		
WI0110-CIF	543	5.0	1.4		
Bi-CIP	330	6.2	3.0		
S-M-S	330	7.2	2.9		
мем	330	5.7	2.9		
11-3-11	543	3.9	1.2		
S-3M	330	3.8	2.9		
S-4M	330	1.7	2.9		

s-w represents the HB between sulfate anion and water, while w-w represents the HB between water molecules. The latter reflects the similar condition of solvent under the same temperature among different ensembles. The data of lifetime are listed in Table S2.

TABLE 4: Data of four sulfate anions in 4S-4M.

Position	S1	S2	S3	S4
Frequency (cm ⁻¹)	983*	1000*	993*	983*
Mg-Os type	1-Bi,1-Mono	2-Mono	2-Mono	2-Mono
Number of HB	2.3	5.0	5.0	4.1

Data end with * were deduced from autocorrelation functions of velocities.

They attributed the shifting to the distortion of SO_4 tetrahedra without further considering the connection of ion-anion interactions or HBs. Interestingly, Raman spectra of MgSO₄ minerals containing different number of hydrated water reveal the same tendency (Figure 6). The *v*-980 mode of kieserite (MgSO₄·H₂O), whose SO₄ groups share same chemical condition of S-4M, is 1046 cm⁻¹, while the frequency of starkeyite (MgSO₄·4H₂O) is 1000 cm⁻¹ with the SO₄ tetrahedra forming 2 Mg-Os bonds and 3 HBs [56].

Given the above, it is difficult to exactly assign each split Raman peak to a certain kind of species. The shift of v-980 mode is significantly determined by the change in SO₄ electron structure due to influence of chemical surroundings. Geofluids



FIGURE 5: Infrared spectra of sulfate anion in different complexes.

TABLE 5:	Vibrational	frequencies	of other	modes.
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Models	<i>T</i> (K)	$V_1 - E ({\rm cm}^{-1})$	$V_2(\text{IR}) - T_2 \text{ (cm}^{-1})$	$V_4(\text{IR}) - T_2 \text{ (cm}^{-1})$
Erro SO	330	438*, 434	609*, (601), 601	(1125), 1126
Fiee 30 ₄	543	441*, 441	609*, (597), 611	1118*, (1111), 1011
Exp. [50] Na ₂ SO ₄	298	449	613	1111
Mono-CIP	330	456*, 445	609*, (605), 605	1111*/1146*, (1115/1146), 1143
	543	446*, 448	607*, 604, 608	1103*/1154*, (1108/1153)
Bi-CIP	330	423*/460*, -	592*/647*, (590/646)	1089*/1134*, (1087/1139/1177)
S-M-S	330	443*, 434	618*, (601), 601	1105*/1140*, (1104/1143), 1146
M-S-M	330	456*, 455	592*, (594), 590/635	1113*/1140*, (1104/1139), 1122
	543	441*, 437	616*, (605), 583/625	1111*/1142*, (-/1146), 1146
S-3M	330		(608)	(1132/1184)
S-4M	330	437	(597), 611	(1160), 1153

Data end with * were deduced from autocorrelation functions of velocities. Data in brackets are from autocorrelation functions of dipoles; others are from autocorrelation functions of polarizabilities.

Wavenumber ~990 cm⁻¹ reflects the existence of one monodentate Mg-Os bond, ~1000 cm⁻¹ can be assigned to the SO₄ tetrahedra associated with 2 Mg^{2+} cations, and ~1005 and 1020 cm⁻¹ are related to the formation of 3 or 4 Mg-Os bonds, respectively. In addition, one bidentate pair of $Mg^{2+}-SO_4^{-2-}$ shows a decrease $\sim 10 \text{ cm}^{-1}$ in wavenumber because of its unbalanced interaction with SO_4 tetrahedra. If one sulfate anion gains both bidentate and monodentate



FIGURE 6: The atomic structure of kieserite, starkeyite, hexahydrite, and epsomite. This picture is generated by VESTA. Black line represents the boundary of unit cell. Color key: Mg = orange; O = red; S = yellow; H = white.



FIGURE 7: Outline of liquid-liquid phase separation of MgSO₄ solution. The light blue background represents water.

CIP associations, the influence on v-980 mode is ambiguous. More cautions should be made to assign Raman peaks to certain associations in other metal-sulfate systems unless integrated with other evidence from AIMD calculations or data of X-ray absorption near edge structure.

4.2. Recognition of Structure in Concentrated Liquid Phase and Phase Separated Process. In liquid-liquid phase separation, chain structure polymers are thought to exist and render Raman peaks ~1020 cm⁻¹ in highly concentrated liquid phase [16, 18]. To our knowledge, Zhang and Chan [15] first proposed the model of chain structure polymers based on experimental Raman spectroscopic measurement, which was further validated by an *ab initio* study [22]. The following studies [16, 18, 24] strengthened the concept. However, because of the limitation of computing cost and undated method of calculating vibrational frequencies in aqueous phase, former simulations suffered from accuracy. Our free energy calculations of CIPs to TIs indicate that longer chains are harder to form in a statistical thermodynamics perspective. Further vibrational calculations of S-3M (1005 cm⁻¹) and S-4M (1020 cm⁻¹) combined with our explanation of ν -980 shift reveal that more complex clusters with S-4M association contribute to peak ~1020 cm⁻¹ in the concentrated liquid phase. As clusters grow larger, the range of 990-1000 cm⁻¹ will be originated from its surface atom, which makes the experimentally counting of relative concentration of species to be quite arbitrary. The monodentate Mg-Os association is dominant in concentrated droplets because monodentate association is more stable than bidentate.

During the whole liquid-liquid phase separated process (Figure 7), CIPs are the major component while TIs present in a relatively small amount at the beginning, based on our analysis of homogeneous phase. CIPs or TIs then gather together to form dehydrated clusters with S-3M or S-4M association. To lower down the system's Gibbs free energy, those clusters would accumulate to form large droplets until they can be measured directly by *in situ* Raman spectra.

Former experiments reveal the temperature and pressure effect on the liquid-liquid phase separation process [16, 18]. With the growth of pressure, the formation temperature of the concentrated liquid phase increases. However, AIMD is limited to small-sized simulations, and the simulation of large cluster is unbearable. Two kinds of classic force field were tested in SI Section 6 (Figure S6) and show poor performance compared to AIMD results. Large-sized simulations based on improved classic force field or machine learning force field deserve further work.

4.3. Relationship between Cluster Formation and Prenucleation Process. The mineralization of magnesium sulfate as well as other sulfate minerals usually happens in epithermalmesothermal hydrothermal deposits or evaporative lakes. Liquid-liquid phase separation has also been found in other sulfate solutions (e.g., ZnSO₄ and CdSO₄) [19, 54]. For a binary CdSO₄-H₂O system, liquid-liquid phase separation would happen at ~473 K. By lowing the pressure and maintaining the temperature, CdSO₄·H₂O crystals precipitate in the concentrated liquid phase [54]. This process is similar to the spinodal decomposition [57], which was proposed for crystallization in supercooling liquid where a trial perturbation triggers nucleation without climbing clear energy barrier (Figure 8). Recurring to the MgSO₄-H₂O system, kieserite (MgSO₄·H₂O) would form at ~543 K under supersaturated concentration based on the phase diagram [16, 58]. The rich concentration liquid phase contains structure units of S-4M association (rendering wavenumber ~1020 cm⁻¹), which shows highly similar chemical environments of SO₄ tetrahedra in kieserite. The S-4M structure in the rich concentration phase acts like the "nuclei" and the crystal grows up around the "nuclei."

Under conditions where spinodal decomposition does not happen spontaneously, in distinction with classical nucleation theory (CNT), a new model emphasizing the importance of prenucleation process [59]-the formation of prenucleation clusters (PNCs) followed by the aggregation of PNCs-has been brought out (Figure 8). For organic materials such as protein, the formation and growth of nanoclusters are directly observed [60]. However, applying this model to mineralization processes still remains debatable. Taking carbonate nucleation as an example, experimental evidence from cryogenic transmission electron microscopic (cryo-TEM) observations [59, 61], MD simulation [20], dielectric relaxation [62], and so forth support the PNC or nanodroplets to be the metastable point during nucleation. But Demichelis et al. [63] and Henzler et al. [64] disagreed with the model of prenucleation process and regarded it to be classical. As the formation of metastable PNC is relatively easy while the energy barrier from liquid to solid is extremely large, to form a metastable structure may not be a decisive step towards crystallization rather than forming a stable nucleus. Besides, different from the cryo-



FIGURE 8: Schematic comparison of prenucleation, CNT, and spinodal decomposition. n represents the number of crystalline molecules, and ΔG is the Gibbs free energy change during nucleation. CNT is a one-step mechanism characterized by a single high free energy barrier (orange). Prenucleation is a two-step pathway with the metastable point representing the liquid precursor (blue). Spinodal decompensation proceeds in a barrierless fashion (yellow).

TEM observation of liquid-liquid separation, the free ions and ion pairs are thought to be dominated rather than PNC aggregation [64].

Similar arguments have been made for calcium sulfate minerals. Reported studies suggested that the formation of sub-3 nm primary species and its coalescence and ordering finally leads to gypsum crystal [65-67]. The main challenge is to confirm the liquid species in supersaturated solutions to settle down the argument. Our studies show the similarity of rich concentration liquid phase and kieserite crystal under high-temperature conditions. Referring to the phase diagram [16, 58] at low temperatures, hexahydrite (MgSO₄·6H₂O) and epsomite (MgSO₄·7H₂O) would precipitate under low supersaturated condition while kieserite (MgSO₄·H₂O) would precipitate under high supersaturated condition. The former two minerals do not have any Mg-Os associations (Figure 6), which accords with reported experimental data [13, 14] of homogeneous solution at low temperatures where CIPs are rare. As mentioned before, for more concentrated solution (>1 M), Raman peaks at ~1005 cm⁻¹ imply the appearance of TIs or larger complexes [15–17]. Our calculation of 4S-4M cluster renders the frequency ~980, 990, and 1000 cm⁻¹ and S-3M renders the frequency ~1004 cm⁻¹ ¹. Those species show same Raman signal of experiments with more complex structure close to kieserite, the aggregation of which may energetically triggers the prenucleation process to form kieserite crystal in concentrated solutions. Investigation for high concentration bulk MgSO₄-H₂O ensembles deserves further work.

5. Conclusions

In our AIMD simulations, the components generating $\sim 1020 \text{ cm}^{-1}$ Raman peak in rich concertation droplets emerging in liquid-liquid phase separated MgSO₄ solution indicate the formation of dehydrated cluster with S-4M association, which is in distinction with chain polymers from

former studies. The similarity between S-4M structure in a concentrated liquid phase and kieserite mineral implies the nucleation pathway of spinodal decomposition. The v-980 shifting in Raman spectra is caused by the changes in the chemical surroundings of SO4 tetrahedra. Wavenumber ~990 cm⁻¹ represents the existence of 1 monodentate Mg-Os bond, $\sim 1000 \text{ cm}^{-1}$ reflects the association with at least 2 Mg^{2+} , and ~1005 and 1020 cm⁻¹ are related to 3 or 4 Mg-Os bonding, respectively. So, we think the split Raman peaks are hardly assigned to certain kind of species because the superposition effects of mixing components are difficult to distinguish. In addition, the free energy curves reveal the stability of Mono-CIP compared to Bi-CIP in homogenous solution at 543 K. However, the *v*-980 mode of Bi-CIP shows a $\sim 10 \text{ cm}^{-1}$ decrease, which makes the Raman spectrum analysis more intricate for systems preferring bidentate associations. Our calculation of liquid species gives an intricate microcosmic view of liquid-liquid phase separation as well as inspirations on mineralization. The autocorrelation method for calculating vibrational frequency presents high accuracy, and it is promising for border application on aqueous system or melts.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

The SI file includes formulas for vibrational frequency calculation, hydrogen bond calculation, and diagrams as a supplement which might be of interest to readers. *(Supplementary Materials)*

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