Research Article

Species of Sulfur in Sour Gas Reservoir: Insights from In Situ Raman Spectroscopy of $S\text{--H}_2\text{S}$\text{--CH}_4$\text{--H}_2\text{O}$ System and Its Subsystems from 20 to 250°C

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Thermochemical sulfate reduction (TSR) is the most important mechanism for the generation of high-concentration $H_2S$ in gas reservoirs. Sulfur speciation in sour gas is one of the key factors controlling the rate and extent of TSR in gas reservoirs. However, experimental studies on $S$ species in sour gas are limited due to the toxicity and corrosion of $S$ and $H_2S$. Fused silica capillary capsules (FSCCs) are inert to $S$ and $H_2S$ and, therefore, were employed in this study as microreactors containing the $S$--$H_2S$--$CH_4$--$H_2O$ system and its subsystems, representing the composition of sour gas. The in situ Raman spectra of each system were collected continuously during the process of heating from 20°C to 250°C. The results showed the following: (1) a Raman peak at 2500 cm$^{-1}$ was detected in the liquid $S$ phase of the $S$--$H_2S$--$CH_4$--$H_2O$ system at 120–250°C, which was attributed to $H_2Sn$. A Raman band at $\sim 533$ cm$^{-1}$ was detected in the aqueous phase of the $S$--$H_2S$--$H_2O$--$CH_4$ system at 250°C and was assigned to $S_3^-$, suggesting that $S_3^-$ and $H_2Sn$ are important $S$ species in sour gas reservoirs at elevated temperatures. (2) The Raman peak at 2500 cm$^{-1}$ disappeared at 20°C, indicating that $H_2Sn$ decomposes into $S$ and $H_2S$. During gas extraction, the decomposition of $H_2Sn$ will cause $S$ deposition in pipelines. (3) In addition to $S_3^-$, $H_2Sn$ could be the intermediate valence $S$ species involved in the TSR reaction.

1. Introduction

Many global deep carbonate gas reservoirs are characterized by elevated $H_2S$ concentrations (i.e., sour gas) [1–5]. $H_2S$ is highly toxic and acidic causing corrosion of pipelines and other metal equipment during gas extractions [6]. In addition, solid $S$ precipitates in pipelines and geological formations, thereby impeding gas production [7]. High concentrations of $H_2S$ and minor amounts of $S$ in natural gas are suggested to be formed during thermochemical sulfate reduction (TSR). It is widely believed that sulfate from evaporates (e.g., anhydrite) is reduced to $S$ and $H_2S$ and these are coupled with the oxidation of hydrocarbons during the TSR reaction [8]. The onset temperature of TSR in gas reservoirs is generally above 120°C [1–3, 5, 9]. However, experimental simulations have estimated the onset temperature to be above 200°C [10–13]. Recently, Truche et al. [14] found that the trisulfur ion ($S_3^-$) is the predominant intermediate valence $S$ species in the TSR reaction in the temperature range of 120–250°C. $S_3^-$ exhibits a catalytic effect on the TSR reaction, lowering the onset temperature and accelerating the rate of TSR [14]. Therefore, to better understand the TSR mechanism, it is important to identify the $S$ species in sour gas.

$S$ has various oxidization states. The $+6$, $+4$, 0, and $-2$ oxidization states are common under normal temperature conditions. At high temperatures, $S$ can also exist in the form of polysulfides, such as $H_2Sn$ [15, 16] and $S_3^-$ [14, 17–20].
Therefore, the S species are more complex at high temperatures than at room temperature. In other words, previous quenching TSR experiments [21–25] could not reflect the true S species under the temperature and pressure (T–P) conditions that exist in deep gas reservoirs, and an in situ approach is needed to improve our understanding of S species in deep gas reservoirs. The presence of S and H₂S can result in the corrosion of metal containers and change the composition of the experimental samples [26, 27]. As a result, in situ high-temperature experiments on S species are quite limited. Experimental investigations on the properties of geological fluids have proven that the use of fused silica capillary capsules (FSCCs) [28, 29] in combination with in situ Raman spectroscopy is a suitable method to study experimental systems containing S and H₂S [14, 30]. FSCCs are made of SiO₂, which is inert to S and H₂S. Raman spectroscopy allows real-time and rapid analysis of the composition of FSCC samples at high temperatures.

The main components of sour gas are CH₄ and H₂S [3]. There are often significant quantities of elemental sulfur dissolved in sour gas at reservoir conditions [31]. To investigate the solubility of elemental sulfur in sour gas, previous investigations focused on the S–H₂S [16] and S–H₂S–CH₄–CO₂ [7, 32] systems. Solid or liquid elemental sulfur can also be encountered in many gas reservoirs where TSR occurred [2, 5, 33–36]. Considering that water is the dominant fluid in the crust [37, 38], the composition of sour gas can be approximated using the S–H₂S–CH₄–H₂O system. The onset temperatures of TSR in global gas reservoirs are generally above 120 °C [2, 3, 9, 39], and the maximum temperatures can reach ~220 °C (e.g., Puguang gas field in Sichuan, China, and Permian Khuff Formation of Abu Dhabi [1, 4]). Therefore, in this study, the reactions within the S–H₂S–CH₄–H₂O system and its subsystems were conducted in FSCCs at temperatures in the range 20 °C to 250 °C to cover the temperature ranges of sour gas reservoirs. In situ Raman spectroscopy was used to characterize the S species at elevated T–P conditions. The contributions of this study include (1) observations on the phase transitions of pure S and H₂S systems at 20–250 °C and the collection of corresponding in situ Raman spectra and (2) the identification of the S species in sour gas reservoirs.

2. Materials and Methods

2.1. Sample Preparation. Rounded cross-sectioned fused silica tubes (793 µm in outer diameter, 203 µm in inner diameter, and 2–4 cm in length; Polymicro Technologies, LLC, United States) were used to construct FSCCs [28, 29]. The chemicals used include powdered solid S (99.8% purity, Sigma-Aldrich, United States), ultra-purified water (18.2 MΩ cm, produced in laboratory), and gaseous CH₄ and H₂S (99.99% purity, Newradar Special Gas Co., Ltd., Wuhan).

The sample-loading system utilized was according to that reported in Chou et al. [28]. Because H₂S is highly corrosive and toxic, a corrosion-resistant type of pressure valves (HiP 15-15AF11HC276) was used [30]. Chou et al. [28] have reported detailed procedures for constructing FSCCs. First, the external protecting polyimide layer of the fused silica tube was removed and one end of the tube was fused by a hydrogen flame. Then, the S powder and liquid water were loaded into the tube, in sequence, through the open end of the tube and centrifuged toward the sealed end. The sealed end was then, immersed in liquid nitrogen, and the open end was connected to the pressure line, which was vacuumized. Gaseous CH₄ and H₂S were subsequently loaded and condensed. Finally, the system was vacuumized, and the open end was sealed by fusion in a hydrogen flame, while the other end was still immersed in liquid nitrogen. The prepared FSCC was about 2 cm long.

2.2. Collection and Processing of In Situ Raman Spectra. Raman spectra were acquired with a high-resolution Raman spectrometer (JY/Horiba LabRAM HR800) using a 532.09 nm laser from an air-cooled, frequency-doubled Nd:YAG laser excitation source, with a 50x objective lens (Olympus), and a 600 groove/mm grating with a spectral resolution of approximately 1 cm⁻¹. The laser was focused on the central level of the horizontal tube, and the laser power reaching the fluid sample was estimated to be ~20 mW, which was sufficient to detect Raman signals of most S species and avoid the fluorescence phenomenon [17]. All spectra were collected from 100 cm⁻¹ to 4000 cm⁻¹ for 5–120 s with 3 accumulations. Before each round of experiments, the v₁ band of silicon at 520.2 cm⁻¹ was used to calibrate the Raman spectrometer.

A heating–cooling stage (CAP500, Linkam Scientific Instruments Ltd.) was used to control the temperature of the FSCCs. The temperature of the heating–cooling stage was calibrated using the triple point (0 °C) and boiling point of water (100 °C), as well as the melting point of NaNO₃ (306.8 °C) at 0.1 MPa. The FSCCs were placed on the heating–cooling stage of the sample chamber, where the temperature range was maintained between ~196 °C and 500 °C. The phase transitions from 20 °C to 250 °C of each sample were observed under an optical microscope. Raman spectra of different phases were collected at temperature points of 20 °C, 50 °C, 100 °C, 150 °C, 200 °C, and 250 °C. The collected spectra were processed using LabSpec (v5.58.25, HORIBA Scientific) software. A linear baseline correction was applied to all spectra. The Raman shifts of S, H₂S, CH₄, H₂O, and other newly formed substances at high temperatures were determined by fitting the spectra using the Gauss–Lorentz function.

3. Results

3.1. Pure S System. An FSCC containing S was heated from 20 °C to 250 °C. Figures 1(a) and 1(b) show the phase transitions of S during heating. At ~115.1 °C, the S powder melted to form liquid S. As shown in Figure 1(c), the solid and liquid S are characterized by intense bands at 153 cm⁻¹, 221 cm⁻¹, and 474 cm⁻¹ and weak bands at 189 cm⁻¹, 250 cm⁻¹, and 441 cm⁻¹ in the 100–500 cm⁻¹ wavenumber range at temperatures of ≤150 °C. With rising temperature, the intense bands at 153 cm⁻¹, 221 cm⁻¹, and 474 cm⁻¹ gradually broadened and shifted to lower wavenumbers, and the weak bands at 189 cm⁻¹, 250 cm⁻¹, and 441 cm⁻¹ were covered by the bands.
at 153 cm\(^{-1}\), 221 cm\(^{-1}\), and 474 cm\(^{-1}\), respectively. These phenomena were reported by Ward [40]. In the 700–1000 cm\(^{-1}\) range, three very weak bands at \(\sim 821\) cm\(^{-1}\), \(\sim 870\) cm\(^{-1}\), and \(\sim 929\) cm\(^{-1}\) were detected at 20–150°C (Figure 1(c)). At 200°C, the broad band from 700 cm\(^{-1}\) to 1000 cm\(^{-1}\) can be deconvoluted into three subbands at 811 cm\(^{-1}\), 861 cm\(^{-1}\), and 913 cm\(^{-1}\). At 250°C, the broad band can be deconvoluted into three subbands at 799 cm\(^{-1}\), 857 cm\(^{-1}\), and 903 cm\(^{-1}\). At temperatures of \(<150°C\), no Raman signal was detected in the vapor phase. At \(\geq 150°C\), three bands at 1248 cm\(^{-1}\), 1439 cm\(^{-1}\), and 1513 cm\(^{-1}\) appeared in the vapor phase (Figure 1(d)).

3.2. Pure \(\text{H}_2\text{S}\) System. Figures 2(a)–2(c) show the phase transitions of the pure \(\text{H}_2\text{S}\) system at temperatures ranging from 20°C to 103.2°C. Vapor and liquid phases coexisted at 20°C (Figure 2(a)). With rising temperatures, the liquid–vapor phase boundary faded away (Figure 2(b)) and homogenized at 103.2°C (Figure 2(c)). As shown in Figure 2(d), the liquid and vapor phases of \(\text{H}_2\text{S}\) were characterized by strong Raman lines at 2578 cm\(^{-1}\) and 2607 cm\(^{-1}\), respectively, at 20°C. The Raman band of vapor \(\text{H}_2\text{S}\) shifted to a lower wavenumber with rising temperature, whereas that of liquid \(\text{H}_2\text{S}\) shifted to a higher wavenumber.

The homogenized fluid phase was characterized by a Raman band at 2595 cm\(^{-1}\) at 150–250°C (Figure 2(e)). At 250°C, a shoulder at 2580 cm\(^{-1}\) was detected. In addition to the strong Raman line at 2595 cm\(^{-1}\), a weak Raman line at \(\sim 1182\) cm\(^{-1}\) was observed in the low-wavenumber region (Figure 2(e)).

3.3. \(\text{S}\)–\(\text{H}_2\text{S}\) System. The liquid and vapor \(\text{H}_2\text{S}\) and solid \(\text{S}\) coexisted at 20°C (Figure 3(a)). At \(\sim 120.0°C\), the solid \(\text{S}\) melted to form liquid \(\text{S}\), and the liquid \(\text{H}_2\text{S}\) homogenized into the vapor phase at 100.6°C. Figure 3(b) shows the coexistence of liquid \(\text{S}\) and vapor \(\text{H}_2\text{S}\).

At low temperatures (e.g., \(<100.6°C\)), the spectra of the solid \(\text{S}\), liquid \(\text{H}_2\text{S}\), and vapor \(\text{H}_2\text{S}\) were comparable with those in the pure \(\text{S}\) and \(\text{H}_2\text{S}\) phases; therefore, these are not illustrated in Figure 3. In addition to the peaks of liquid \(\text{S}\), two new bands at \(\sim 2500\) cm\(^{-1}\) and 2570 cm\(^{-1}\) were detected at \(\geq 120°C\) (Figure 3(c)). In the vapor phase, only the \(\sim 2600\) cm\(^{-1}\) peak of \(\text{H}_2\text{S}\) was observed, whereas the new peaks at \(\sim 2500\) cm\(^{-1}\) and 2570 cm\(^{-1}\) were not observed (Figure 3(d)). Raman spectra of the solid \(\text{S}\) were collected...
when the samples were quenched from 250°C to 20°C. The band at 2500 cm\(^{-1}\) disappeared, whereas that at 2570 cm\(^{-1}\) still existed but shifted slightly to 2567 cm\(^{-1}\) in the quenched solid S (Figure 3(c)).

3.4. S–H\(_2\)S–CH\(_4\) System. The phase transitions in the ternary S–H\(_2\)S–CH\(_4\) system were comparable with those in the pure S and H\(_2\)S systems and the binary S–H\(_2\)S system; thus, they are not further illustrated in Figure 4. At >123°C, this system was composed of liquid S and the vapor phase. Figures 4(a) and 4(b) show the in situ Raman spectra of the liquid and vapor phases of the S–H\(_2\)S–CH\(_4\) system at 150–250°C and 20°C (quenched). In the high-wavenumber region, the liquid phase was characterized by three Raman bands at ~2500 cm\(^{-1}\), 2570 cm\(^{-1}\), and 2895 cm\(^{-1}\) (Figure 4(a)). Raman spectra of quenched solid S showed that the band at 2500 cm\(^{-1}\) disappeared, whereas that at 2570 cm\(^{-1}\) still existed but was shifted slightly to 2567 cm\(^{-1}\) at 20°C (Figure 4(a)). In the vapor phase, the 2605 cm\(^{-1}\) band and the left-hand shoulder at 2580 cm\(^{-1}\) were detected, which are similar to those in the pure H\(_2\)S system (Figures 2(e) and 4(b)). A strong Raman band at ~2914 cm\(^{-1}\) and two weak bands at 3013 cm\(^{-1}\) and 3069 cm\(^{-1}\) were also identified, which were ascribed to the presence of CH\(_4\). In the H\(_2\)S–CH\(_4\)–N\(_2\) system, no liquid H\(_2\)S was observed at 20°C. Except for a weak Raman band at 2327 cm\(^{-1}\), the other bands could also be observed in the vapor phase of the S–H\(_2\)S–CH\(_4\) system (Figures 4(b) and 4(c)). Therefore, the 2327 cm\(^{-1}\) band should have arisen from the vibration of N\(_2\).

3.5. S–H\(_2\)S–H\(_2\)O System. At 20°C, the S–H\(_2\)S–H\(_2\)O system contained solid S, the aqueous phase, and vapor phase (Figure 5(a)). At temperatures above 110°C, the solid S melted to form liquid S and coexisted in the aqueous and vapor phases (Figure 5(b)). In the liquid S, Raman bands at 2500 cm\(^{-1}\) and 2570 cm\(^{-1}\) were observed at >110°C, and the 2500 cm\(^{-1}\) band disappeared in the quenched sample (Figure 5(c)). In the vapor phase, a strong Raman band of H\(_2\)S was observed at ~2604 cm\(^{-1}\) (Figure 5(d)). In addition, the Raman band of vapor H\(_2\)O was detected at ~3644 cm\(^{-1}\) at ≥150°C. The Raman band at 2327 cm\(^{-1}\) was ascribed to N\(_2\) in the air. In the aqueous phase, the most prominent Raman bands were from dissolved H\(_2\)S (~2582 cm\(^{-1}\)) and liquid water (~1630 cm\(^{-1}\) and ~2800–3800 cm\(^{-1}\)) (Figure 5(e)). A new Raman band at ~533 cm\(^{-1}\) was detected after heating at 250°C for 4 h, which disappeared in the quenched sample (20°C) (Figure 5(e)).
3.6. S–H₂S–CH₄–H₂O System. At 20°C, the S–H₂S–CH₄–H₂O system contained solid S, vapor H₂S and CH₄, and aqueous phases. At >114.7°C, this system was characterized by the coexistence of liquid S, vapor, and aqueous phases. The phase transitions of the S–H₂S–CH₄–H₂O system were similar to the systems investigated in the previous sections; hence, they are not further illustrated in Figure 6.
Besides the CH\textsubscript{4} bands, the Raman spectra of this system were similar to those for the S–H\textsubscript{2}S–H\textsubscript{2}O system at 150–250°C (Figures 5 and 6). In the liquid S phase, three bands at ~2498 cm\textsuperscript{-1}, 2568 cm\textsuperscript{-1}, and 2895 cm\textsuperscript{-1} were observed, which were similar to those detected in the S–H\textsubscript{2}S–CH\textsubscript{4} system (Figures 4(a) and 6(a)). In the vapor phase, the Raman bands of H\textsubscript{2}S and water were centered at ~2603 cm\textsuperscript{-1} and 3642 cm\textsuperscript{-1}, respectively (Figure 6(b)). The major CH\textsubscript{4} band was centered at ~2914 cm\textsuperscript{-1}, and two additional weak bands appeared at higher wavenumbers. The weak 2327 cm\textsuperscript{-1} band was ascribed to atmospheric N\textsubscript{2}. In the aqueous phase, in addition to the 2327 cm\textsuperscript{-1} (dissolved atmospheric N\textsubscript{2}) and 2907 cm\textsuperscript{-1} bands, other Raman bands that were comparable with those observed in the S–H\textsubscript{2}S–H\textsubscript{2}O system were also present (Figures 5(e) and 6(c)).

4. Discussion

4.1. Identification of Polysulfides

4.1.1. Raman Spectra of S, H\textsubscript{2}S, CH\textsubscript{4}, and H\textsubscript{2}O. For the Raman spectra of S, the Raman bands at 153 cm\textsuperscript{-1}, 220 cm\textsuperscript{-1}, and 474 cm\textsuperscript{-1} were assigned to the \nu\textsubscript{6}, \nu\textsubscript{2}, and \nu\textsubscript{1} vibrations, respectively [41]. The other minor bands include
the $\nu_6$ vibration at 188 cm$^{-1}$, $\nu_{11}$ vibration at 251 cm$^{-1}$, and $\nu_{10}$ vibration at 441 cm$^{-1}$ (Figure 1(c)) [41]. The $\nu_1$ and $\nu_{10}$ bands represent the stretching vibration of the S–S bond, whereas the $\nu_2$, $\nu_5$, $\nu_9$, and $\nu_{11}$ bands represent the bending vibration of the S–S–S bond [42]. The weak bands at 821 cm$^{-1}$, 870 cm$^{-1}$, and 929 cm$^{-1}$ in the 800–1000 cm$^{-1}$ region are combination bands and overtone bands for S (Figure 1(c)) [42]. The Raman peaks at 1248 cm$^{-1}$ and 1439 cm$^{-1}$ were detected in the vapor and aqueous phases of the S–H$_2$O system at ≥170°C [13]; however, they were assigned to unknown S-bearing species. In this study, besides the 1248 cm$^{-1}$ and 1439 cm$^{-1}$ bands, the Raman band at 1513 cm$^{-1}$ was observed in the Raman spectra of the vapor phase for the pure S system at ≥150°C (Figure 1(d)). As only S is present in the sample, the bands at 1248 cm$^{-1}$, 1439 cm$^{-1}$, and 1513 cm$^{-1}$ should be attributed to it, although details on vibrational modes are not clear at present.

Based on the Raman spectra of H$_2$S, the predominant band at 2500–2700 cm$^{-1}$ was assigned to the symmetrical S–H stretching vibration ($\nu_1$) [30, 43]. The $\nu_1$(H$_2$S) Raman shift could be used to measure the H$_2$S density [30]. Therefore, the $\nu_1$(H$_2$S) bands of coexisting liquid and vapor H$_2$S were characterized by distinct peak positions at a constant temperature (Figure 2(d)) as the liquid and vapor phases have different densities. The variation in the $\nu_1$(H$_2$S) band position indicates an increase in the fluid density of the vapor
phase and a decrease in the liquid phase density with rising temperature [30]. After the homogenization of the liquid and vapor H$_2$S, the bulk density of H$_2$S remained constant when the expansion of the FSCC was neglected. As a result, the $\nu_1$ band of the homogeneous H$_2$S phase did not show an obvious shift with rising temperature (Figure 2(e)) [44]. The shoulder at 2580 cm$^{-1}$ was detected at elevated temperatures and could be assigned to the hot band (Figure 2(e)) [30].

In the vapor phases of the S–H$_2$S–CH$_4$–H$_2$O systems, the ~2914 cm$^{-1}$, ~3066 cm$^{-1}$, and ~3016 cm$^{-1}$ bands (Figures 4(b), 4(c), and 6(b)) were assigned to the $\nu_1$, $2\nu_2$, and $\nu_3$ vibrations of CH$_4$, respectively [45]. The 2895 cm$^{-1}$ band was detected in the liquid S of the S–H$_2$S–CH$_4$ system (Figure 4(a)), and the 2907 cm$^{-1}$ band was detected in the aqueous phase of the S–H$_2$S–CH$_4$–H$_2$O system (Figure 6(c)). Both bands are located in the C–H stretching vibration region [46–48]. Since the only hydrocarbon existing in the samples was CH$_4$, the bands at 2895 cm$^{-1}$ and 2907 cm$^{-1}$ were assigned...

**Figure 6:** *In situ* Raman spectra for the S–H$_2$S–CH$_4$–H$_2$O system at 150–250°C. (a) Liquid S phase, (b) vapor phase, and (c) aqueous phase. Raman spectra of the quenched sample (20°C) are also shown for comparison. Stars denote the background signals of the silica tube.
to CH$_4$ dissolved in liquid S and water, respectively. The intermolecular interactions between CH$_4$ and the solvent altered the intramolecular potential energy of CH$_4$, and thus, the v$_1$(CH$_4$) band shifted to the lower wavenumber [49–51]. In water-bearing systems, the ~1630 cm$^{-1}$ and 3000–3800 cm$^{-1}$ bands were ascribed to the O–H bending and stretching vibrations, respectively, of liquid water (Figures 5(e) and 6(c)) [52]. The narrow ~3642 cm$^{-1}$ band in the vapor phase at elevated temperatures was assigned to the O–H stretching vibration of water vapor (Figures 5(d) and 6(b)) [47]. The ~2327 cm$^{-1}$ band in the vapor phases of the H$_2$S–CH$_4$–H$_2$O, S–H$_2$S–H$_2$O, and S–H$_2$S–CH$_4$–H$_2$O systems was assigned to the N–N stretching vibration of N$_2$ (Figures 4(c), 5(d), and 6(b)) [53].

4.1.2. Raman Spectra of H$_2$Sn. Compared with the Raman spectra of pure S and H$_2$S systems (Figures 1 and 2), the liquid S phase of the S–H$_2$S system was characterized by two new bands at 2500 cm$^{-1}$ and 2570 cm$^{-1}$ (Figure 3(c)), indicating the formation of some new components. The 2500 cm$^{-1}$ and 2570 cm$^{-1}$ bands were also observed in the liquid S phase of the S–H$_2$S–H$_2$O, S–H$_2$S–CH$_4$, and S–H$_2$S–H$_2$O–CH$_4$ systems at 150–250°C (Figures 4(a), 5(c), and 6(a)), suggesting that the new substances were also stable in the presence of CH$_4$ and H$_2$O. After cooling from 250°C to 20°C, the 2500 cm$^{-1}$ band completely disappeared; however, the band at 2570 cm$^{-1}$ was still detected, but shifted slightly to 2567 cm$^{-1}$ (Figures 3(c), 4(a), 5(c), and 6(a)). Therefore, the two Raman bands represent the vibrational modes of different species.

For the ~2500 cm$^{-1}$ band in liquid S (Figures 3(c), 4(a), 5(c), and 6(a)), previous studies have shown that the vibration of H$_2$S$_n$ (n ≥ 2) is in the 2480–2560 cm$^{-1}$ range [54–57]. H$_2$S$_n$ (n ≥ 2) can be generated by the reaction between liquid S and dissolved H$_2$S [58]:

$$\text{H}_2\text{S} + n\text{S}_{\text{aq}} \rightarrow \text{H}_2\text{S}_n + 1.$$  \hspace{1cm} (1)

H$_2$S$_n$ (n ≥ 2) is thermally unstable and decomposes with a drop in T–P [58]:

$$\text{H}_2\text{S}_n \rightarrow \frac{n-1}{8}\text{S}_8 + \text{H}_2\text{S}.$$  \hspace{1cm} (2)

Previous studies have reported the existence of the ~2500 cm$^{-1}$ and ~2570 cm$^{-1}$ bands in the spectra of S-bearing systems [15, 45, 59]. For the former band, Wiewiorowski and Touro [15] reported the infrared spectra of the S–H$_2$S system at 125–181°C and ascribed it to the formation of H$_2$S$_n$ by the interaction of H$_2$S with liquid S. The ~2500 cm$^{-1}$ band was also observed in natural fluid inclusions containing S and H$_2$S [45, 59]. Hurai et al. [45] believed that the ~2500 cm$^{-1}$ band was related to H$_2$S$_2$ dissolved in solid sulfur. H$_2$S$_2$ was generated by the reaction between molten S and the surrounding H$_2$S-rich fluid.

In our experiment, the Raman spectra of liquid S in systems containing S and H$_2$S revealed a band at ~2500 cm$^{-1}$ at 120–250°C (Figures 3(c), 4(a), 5(c), and 6(a)), suggesting the generation of H$_2$S$_n$ according to Equation (1). The ~2500 cm$^{-1}$ band was not observed in solid S in the quenched samples at 20°C (Figures 3(c), 3(d), and 5(c)), indicating the decomposition of H$_2$S$_n$ according to Equation (2). Based on the above discussion, the ~2500 cm$^{-1}$ band in the S–H$_2$S–H$_2$O–CH$_4$ systems was assigned to H$_2$S$_n$ (n ≥ 2).

For the ~2570 cm$^{-1}$ band in liquid S (Figures 3(c), 4(a), 5(c), and 6(a)), there have been different interpretations in previous studies [15, 45]. Wiewiorowski and Touro [15] assigned the band to dissolved H$_2$S in liquid S, whereas Hurai et al. [45] believed that this band was associated with the S–H stretching vibration of H$_2$S + H$_2$S$_2$ dissolved in sulfur. In our experiment, the ~2570 cm$^{-1}$ component existed in solid S in the quenched samples containing S and H$_2$S (Figures 3(c), 4(a), 5(c), and 6(a)). This is different from H$_2$S$_n$ whose Raman signal disappeared at room temperature. Therefore, we believe that the band at 2570 cm$^{-1}$ is associated with dissolved H$_2$S in liquid S at high temperatures instead of H$_2$S$_n$.

4.1.3. Raman Spectra of S$_3^-$. The trisulfur ion S$_3^-$ has been shown to be one of the most important S species in hydrothermal fluids [14, 17–19]. The characterized Raman bands of S$_3^-$ are from its S–S symmetric stretching mode at 538 ± 5 cm$^{-1}$ and the corresponding overtones at ~1076 cm$^{-1}$ and ~1606 cm$^{-1}$ [17]. The Raman band at ~533 cm$^{-1}$ was observed in the aqueous phases of the S–H$_2$S–H$_2$O and S–H$_2$S–H$_2$O–CH$_4$ systems at 250°C (Figures 5(e) and 6(c)), indicating the presence of S$_3^-$ ions. Signals of the overtones of S$_3^-$ at ~1076 cm$^{-1}$ and ~1606 cm$^{-1}$ might be too weak and overlapped by the intense bands of the silica tube (~1060 cm$^{-1}$) and water (~1630 cm$^{-1}$).

Conditions favoring the formation of S$_3^-$ include a suitable redox state (e.g., the presence of SO$_4^{2-}$ and H$_2$S), an acidic solution (pH = 1.2–6), and elevated temperatures (e.g., 200–350°C) [14]. SO$_4^{2-}$ and HSO$_4^-$ were initially absent in the S–H$_2$S–H$_2$O systems; however, they could be generated through the disproportionation of S, which was reported to happen in the S–H$_2$O system at temperatures of >200°C [60]:

$$4\text{S}_{(l)} + 4\text{H}_2\text{O}_{(l)} \rightarrow \text{HSO}_4^- + 3\text{H}_2\text{S}_{(aq)} + \text{H}^+.$$  \hspace{1cm} (3)

Therefore, minor sulfate (i.e., below the detection limit of the Raman spectrometer) was generated in the S–H$_2$S–H$_2$O and S–H$_2$S–H$_2$O–CH$_4$ systems at 250°C. Then, S$_3^-$ was formed through the reaction between sulfate and H$_2$S.

4.2. Sulfur Species in Sour Gas. Previous observations showed that the predominant S species in gas reservoirs are H$_2$S in the vapor phase, SO$_4^{2-}$ and H$_2$S in the aqueous phase, and anhydrate, S, and pyrite in the solid phase [3, 9, 61]. Our study suggests that H$_2$S$_n$ and S$_3^-$ are also important S species under reservoir temperature conditions with the presence of abundant elemental sulfur. H$_2$S$_n$ is stable in the S–H$_2$S–CH$_4$–H$_2$O system over a wide temperature range (i.e., 150–250°C).
and is enriched in liquid S (Figure 6(a)). S exists in the liquid state at temperatures >120°C in the gas reservoirs. In addition, H2S is a common component of natural gas. Thus, H2Sn could be generated according to Equation (1) and enriched in deep gas reservoirs. Besides, some previous studies also support the presence of H2Sn in petroleum reservoirs. For example, Langer and Hyne [62] reported that H2Sn was the intermediate product of the reaction between mercaptans and liquid S at 130°C. Hurai et al. [45] and Tritilla et al. [59] detected the Raman signal of H2Sn in natural fluid inclusions containing S, H2S, and CH4.

Dissolved H2S and S2− were observed in the aqueous phases of the S–H2S–H2O and S–H2S–H2O–CH4 systems at 250°C, whereas H2Sn−, HS−, and Sn2− were absent in the aqueous phases (Figures 5(e) and 6(c)). This result can be interpreted as follows: (a) H2Sn preferentially dissolves in liquid S instead of water, and (b) very little H2Sn was generated, and thus, the concentration of dissolved H2Sn in the aqueous phase was below the detection limit of the Raman spectrometer.

In the vapor phase, only H2S, CH4, and H2O were detected in the S–H2S–H2O–CH4 system (Figure 6(b)). However, the Raman signals of S and H2Sn were not detected. In contrast, the experimental results of Migdisov et al. [16] support the presence of gaseous S and H2Sn (n = 2−5) in the vapor phase of the S–H2S system at 200–290°C. The boiling points of H2S and H2Sn are 70.7°C and 90°C, respectively [63]. Thus, a small concentration of H2Sn exists in the vapor phase of the S–H2S–H2S–CH4, S–H2S–H2O, and S–H2S–CH4–H2O systems at elevated temperatures (i.e., ≥200°C). The plausible explanation for our finding is that the contents of gaseous S and H2Sn generated in the S–H2S–H2O–CH4 system are below the detection limit of the Raman spectrometer. Nevertheless, H2Sn and S should be the S species in the vapor phase when the vapor–liquid equilibrium is taken into account.

S deposition in geological formations and gas wells may reduce well productivity and corrode metal equipment during the extraction of natural gas [7]. Our observations indicate that H2Sn decomposes into H2S and S with decreasing sample temperature (Figures 3(c), 4(a), 5(c), and 6(a)). Therefore, the decomposition of H2Sn may be one of the mechanisms of S deposition [58, 64].

S species with intermediate valences, such as thiols, S, and S2−, have high reactivity, promoting the TSR reaction [8, 12–14]. S2− can be stable at temperatures of up to 700°C [65]. Furthermore, it is especially important that S2− can even be present at temperatures as low as 100°C in the (NH4)2SO4–H2S–H2O system [14]. S2− was also found in natural fluid inclusions at temperatures above 100°C [19]. The temperature range of methane-dominated TSR in natural systems was proposed to be 135−200°C [1, 3, 5, 9, 34, 66, 67]; therefore, it is highly possible that S2− is present in deep (>3 km) sour gas reservoirs.

However, H2Sn− was not identified in previous experiments in which S2− was reported [14, 17, 19]. Our study indicates that H2Sn− is stable at 120–250°C, which is the temperature interval for the occurrence of the geological TSR reaction [1−5, 9]. S2− and H2Sn− coexist in the S–H2S–H2O and S–H2S–CH4–H2O systems at 250°C (Figures 5(e) and 6(c)), indicating that H2Sn− and S2− may coexist in deep gas reservoirs at elevated temperatures. H2Sn− are much stronger acids in water than H2S [68]. The presence of H2Sn− in gas reservoirs may thus contribute to an acidic environment, which is favorable for the acceleration of TSR [69]. Moreover, H2Sn− are highly unstable and reactive molecules, known to be strong nucleophiles and reductants. H2Sn− are expected to be more reactive in certain nucleophilic reactions than H2S or thios [70]. H2Sn molecules dissociate to form HS− and Sn2− in aqueous solutions [71, 72]. HS− and Sn2− are stronger nucleophiles than H2S and easily react with organic matter to form organic polysulfides [73–76]. R–Sn− is detected in crude oil from the Sichuan Basin (southwestern China) [77] and the Tarim Basin (northwestern China) [78]. The presence of R–Sn− is ascribed to the interaction between aldehydes and reactive nucleophilic HS−. H2Sn dissociates to form HS− [71, 72]. Then, H2Sn might react with hydrocarbon to form the intermediate product of TSR, promoting the TSR reaction.

4.3. Other Implications. In addition to carbonate reservoirs [59, 79], S and H2S are common components of magmatic–hydrothermal systems, such as crater lakes [80], hot springs [81], and submarine volcanoes [82]. Our results support the presence of H2Sn− in magmatic–hydrothermal systems. This conclusion is also supported by the observations of Takano et al. [80], who presented evidence for the presence of H2Sn in molten S slick, and Pokrovski and Dubessy [18], who quantified the stability and abundance of S2− under hydrothermal conditions.

Magmatic–hydrothermal fluids are important for the formation of ores. Formation of polysulfide complexation can influence the transport and deposition of ore elements (e.g., As [83] and Au [65, 84]) in magmatic–hydrothermal fluids. Thus, the effects of polysulfides on the formation of magmatic–hydrothermal deposits need to be explored further.

5. Conclusions

Fused silica capillary capsules (FSCCs) containing the S–H2S–CH4–H2O system and its subsystems were prepared. The FSCCs were heated from 20°C to 250°C, and the corresponding in situ Raman spectra were obtained. The major contributions of this study include the following:

(1) The in situ Raman spectra of H2S and S at elevated temperatures were presented, and the formations of H2Sn− and S2− in the S–H2S–CH4–H2O system were revealed. The Raman band at ~2500 cm−1 in liquid S indicates the presence of H2Sn− in the S–H2S–H2O–CH4 system over a wide temperature range of 120–250°C. The Raman band at ~533 cm−1 indicates the presence of S2− in the S–H2S–H2O–CH4 system at 250°C.

(2) H2Sn− and S2− were recognized as important S species in sour gas reservoirs in addition to sulfate, S, H2S, and sulfides. H2Sn− is thermally unstable, easily decomposes to form S and H2S, and causes S
deposition. $\text{H}_2\text{S}_n$ and $\text{S}_n^-$, as intermediate valence S species, might take part in and promote the TSR reaction in gas reservoirs.

(3) The effects of $\text{H}_2\text{S}_n$ and $\text{S}_n^-$ on the transport and precipitation of ore elements were emphasized. $\text{S}$ and $\text{H}_2\text{S}$ are common components in the magmatic-hydrothermal system. Previous studies have confirmed the presence of polysulfide in hydrothermal fluids. The effects of $\text{H}_2\text{S}_n$ and $\text{S}_n^-$ on the mineralization of some ore elements should be further investigated.

Data Availability

All data used to support the findings of this study are available from the corresponding authors on request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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