Raman vibrational spectral characteristics and quantitative analysis of H$_2$ up to 400°C and 40 MPa

Lianfu Li$^{1,2,3}$ | Xin Zhang$^{1,2,3}$ | Zhendong Luan$^{1,2}$ | Zengfeng Du$^1$ | Shichuan Xi$^{1,3}$ | Bing Wang$^{1,3}$ | Lei Cao$^1$ | Chao Lian$^1$ | Jun Yan$^1$

1 CAS Key Laboratory of Marine Geology and Environment & Center of Deep Sea Research, Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China
2 Laboratory for Marine Geology, Qingdao National Laboratory for Marine Science and Technology, Qingdao, China
3 University of Chinese Academy of Sciences, Beijing, China

Abstract
In situ Raman detection is an ideal method to determine the concentration of dissolved H$_2$ in deep-sea high temperature hydrothermal fluids, but studies on in situ Raman qualitative and quantitative analyses of H$_2$ that are suitable for detection in high temperature hydrothermal fluids are lacking. In this study, the Raman characteristics of gaseous and dissolved H$_2$ were researched at 0–400°C and 0–40 MPa in detail, which cover most deep-sea hydrothermal environments. The strong density and temperature dependences of the wavenumber and bandwidth of gaseous hydrogen vibrational Raman bands were observed. The interactions between the water molecules and hydrogen molecules were affected by temperature and pressure, and the opposite effect on the vibrational band of dissolved hydrogen was observed before and after reaching the critical condition of water. A high temperature and pressure quantitative analysis model suitable for in situ Raman detection of dissolved H$_2$ was also developed with the linear equation $A_{H2}/A_{H2O} = 1.437 \times C_{H2}$, where $A_{H2}/A_{H2O}$ is the peak area ratio of H$_2$ and H$_2$O, and $C_{H2}$ is the concentration of dissolved H$_2$ in mol/kg. The experimental temperature and pressure conditions did not influence the linear trend between the peak area ratio of $A_{H2}/A_{H2O}$ and the concentrations of H$_2$, which indicated that the calibration model can be applied to high temperature and pressure environments.

KEYWORDS
deep-sea, hydrogen, hydrothermal vent fluid, in situ, quantitative analysis

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1 | INTRODUCTION

H₂ is an important gas species in deep-sea hydrothermal fluids, and its production is generally considered to include biological and nonbiological processes. The biological hydrogen production processes mainly consist of organic matter fermentation and anaerobic oxidation of carbon monoxide. Nonbiological hydrogen production processes include mantle degassing, the low-temperature reactions associated with active fault activity, basaltic magma crystallization, and the serpentinization reaction, which is the dominant hydrogen production reaction in hydrogen-rich hydrothermal vents. Although the hydrogen generation reaction is widespread, the concentration of H₂ in hydrothermal fluid is very low (0.1–0.6 mmol/kg in basalt-hosted hydrothermal fields), and its volume fraction is less than 2%. However, in ultramafic-hosted hydrothermal fields (e.g., Rainbow, Logatchev 1, Logatchev 2, Lost City, Ashadze 1, and Ashadze 2), the hydrogen gas component can exceed 40%, and the concentration of H₂ can reach 8–19 mmol/kg. In the Ashadze 2 hydrothermal field, hydrogen accounts for 76.5% of the gas component, and the concentration of dissolved hydrogen can reach 26.5 mmol/kg. The H₂ fluxes of the slow spreading ridge and mid-ocean ridge are estimated to be approximately 89 × 10⁹ mol/year and 133 × 10⁹ mol/year, respectively. Therefore, research on the global hydrogen cycle should not ignore the contribution of hydrothermal vents in the ocean.

However, there are still no effective measurement devices (e.g., H₂ sensors) to in situ detect and determine accurate H₂ concentrations in hydrothermal fluids because of their high temperature, high pressure, and corrosion environments. Although traditional sampling methods (e.g., gas-tight sampling) can maintain the high pressure conditions of deep-sea, the measurement uncertainties due to the changes in both temperature and in situ environment cannot be avoided. The deployment of in situ Raman spectrometers, RiP and DORISS, provides an effective method to solve this difficulty for their nondestruction, noncontact, and suitable for liquid environment characteristics. Many studies have shown that in situ Raman detection is a useful and reliable method for qualitative and quantitative analyses in the deep ocean. We have collected some in situ Raman spectra of high temperature hydrothermal fluids using the RiP system, and potential Raman hydrogen peaks were observed in the in situ Raman spectra. To assign the potential Raman hydrogen peak and to determine the concentration of H₂ in high temperature hydrothermal fluids, qualitative and quantitative Raman analyses on hydrogen suitable for in situ Raman detection of high temperature hydrothermal fluids must be performed.

The characteristics of hydrogen Raman spectra reflect the motion states of the molecules and intermolecular interactions, which are sensitive to the temperature and pressure. May et al. first systematically researched the Raman characteristics of hydrogen under varying pressures (up to 200 MPa) at room temperature through a series of studies. Raman spectra of hydrogen under high and ultrahigh pressure conditions were researched by Sharma et al. (up to 63 GPa), Mao et al. (up to 147 GPa), and Gregoryanz et al. (up to 150 GPa). Rahn et al. and Bischel and Dyer calculated the temperature and density dependence of peak position and the line width of hydrogen at the condition up to 1,100 K and 5 MPa. The Raman spectra of dissolved hydrogen in water or other solvents (such as SF₆, CCl₄, and ScCO₂) are quite different from those of pure H₂ system because of solute–solvent interactions. The vibrational Raman spectra of dissolved H₂ in pure water at high pressures up to 110 MPa and 200 MPa under low temperature conditions were researched by Ziparo et al. and Borysow et al. respectively. Although numerous studies about Raman spectra of hydrogen have been reported, either these experimental temperature and pressure conditions are too high or too low or the experimental temperature and pressure intervals are too large to cover in detail the environment of hydrothermal fluids, which generally are under conditions of 0–40 MPa and 0–400°C.

In this study, an extreme environment simulator was built to simulate high temperature hydrothermal fluid environments. The Raman characteristics of gaseous and dissolved H₂ in pure water and seawater were systematically explored in the temperature and pressure ranges of 0–400°C and 0–40 MPa. In addition, to quantify the dissolved H₂ content using in situ Raman spectra, the quantitative calibration model suitable for dissolved H₂ under high temperature and pressure conditions was established.

2 | DEVICES AND METHODS

2.1 | Deep-sea extreme environment simulator

The simulator with a volume of approximately 6 ml was composed of Hastelloy alloy, which can withstand 400°C and 45 MPa conditions and strong acid and alkaline fluid corrosion for a long time (Supporting Information Figure S1). The head of the Raman reactor designed a round hole for the custom-built Raman immersion probe (Kaiser Optical Systems, Inc., Ann...
Arbor, USA), which could work at temperatures and pressures up to 450°C and 70 MPa, respectively. A MultiRxn probe (Kaiser Optical Systems, Inc.) connected to the immersion probe was used to collect the Raman spectra. Between the head of the reactor and the immersion probe, a polytetrafluoroethylene O ring (can withstand temperatures up to 320°C) was used to ensure an airtight environment. The pressure of the simulator could be maintained with a precision of 0.05 MPa in the range of 0–45 MPa. The Raman reactor was heated/cooled using a thermoelectric refrigeration system with a temperature control range of −20–80°C and a temperature stability of ±0.1°C.[49]

2.2 | Raman spectrometer

The Raman acquisition equipments used to carry out the qualitative and quantitative analyses were based on the RiP system[27] using a custom-designed N-RXNEX-532-RA-SP spectrometer (Kaiser Optical Systems, Inc.) and a DU-440A-BV-136 charge-coupled device (Andor Technology, Inc., South Windsor, CT, USA) with 2,048 × 512 pixels and a 27.6 × 6.9-mm image area. The spectra in the range of 100–4,325 cm⁻¹ were split into two lines by the multiplexed grating, and the spectral resolution of the Raman spectrometer was approximately 1 cm⁻¹ per pixel. Despite the spectral resolution of our experimental setup is 1 cm⁻¹, the difference of repetitive measurement to the sample with same condition is less than ±0.02 cm⁻¹. The excitation source was a frequency doubled Nd: YAG laser (532 nm; Kaiser Optical Systems, Inc.) with an output power of 150 mW. The Raman spectrometer was connected to the MultiRxn probe through two 100-μm-diameter fibers. Neon and halogen lamps were used to calibrate the wavenumber and intensity of the Raman spectrometer, respectively.

2.3 | Raman spectra processing

The Raman spectra of the samples were collected using the software HoloGRAM (Kaiser Optical Systems, Inc.) in the range of 100–4,325 cm⁻¹ with an exposure time of 3 s and four accumulations. In addition, the spectrum for each sample was acquired 3 times in succession under the same temperature and pressure conditions. The software GRAMS/AI (Thermo Fisher Scientific, Inc., Waltham, USA) was used for the baseline calibration of the Raman spectra. The peak position, full width at half maximum (FWHM), and peak area were determined by the GRAMS/AI peak-fitting routine.

2.4 | Chemical preparation

To research the Raman characteristics of gaseous H₂, the gaseous H₂ (Airtec Gas Co. Ltd., Qingdao, China; purity >99.9%) was pumped into the reactor by a gas supercharging system. To research the Raman characteristics of dissolved H₂ and establish the quantitative model for dissolved H₂ under high temperature and pressure conditions, ultrapure water and standard seawater (35‰; National Center of Ocean Standards and Metrology, Tianjin, China) were pumped into the reactor through a liquid supercharging system.

3 | RESULTS AND DISCUSSION

The rotational and vibrational Raman lines for gaseous and dissolved H₂ in pure water are shown in Figure 1. S₀ (1), S₀ (3) and Q₁ (1), Q₁ (3) correspond to the rotational and vibrational Raman bands of the ortho-hydrogen, respectively. S₀ (0), S₀ (2) and Q₁ (0), Q₁ (2) correspond to the rotational and vibrational Raman bands of para-hydrogen, respectively.[36–39] In this study, only the vibrational Raman spectra of gaseous and dissolved H₂ were systemically researched for the pure rotational lines are erased in dissolved H₂ Raman spectra.

3.1 | Raman characteristics of H₂ vibrational spectra

3.1.1 | Gaseous H₂

The wavenumber shifts in the Q-branch for gaseous H₂ are shown in Figure 2 and Supporting Information.
Figure S2. Under the conditions of 0–400°C and 0–40 MPa, the Q1 (0) band is not sensitive to temperature changes. The Raman Q1 (0) lines fluctuated less than 0.2 cm⁻¹ as the temperature increased from 50°C to 400°C (Figure 2). The intensity of the Q1 (0) band is very weak; thus, the peak-fitting procedure will result in large uncertainties. In addition, based on the resolution of the Raman spectrometer, determining a redshift or blueshift in the Q1 (0) lines as the temperature changes is difficult. In contrast to the temperature, the pressure has an obvious effect on the wavenumbers of Q1 (0) band. The peak positions of Q1 (0) band shifted to lower wavenumbers by approximately 0.4 cm⁻¹ as the pressure increased from 5 to 40 MPa (Figure S2). Compared with its effect on Q1 (0), the effects of temperature on the peak positions of Q1 (1), Q1 (2), and Q1 (3) bands were significant, and their changes are shown in Figure 2. A positive relationship between the temperature and the Raman wavenumbers of Q1 (1), Q1 (2), and Q1 (3) bands was found. The relationship was also affected by the pressure—specifically, the slope of the relationship became larger with increasing pressure (Figure 2). The same positive relationship was also found between the pressure and Raman wavenumbers of the Q1 (1), Q1 (2), and Q1 (3) bands (except those for Q1 (1) at 50°C and 100°C), and the slope of the relationship became larger as the temperature increased (Supporting Information Figure S2).

The Q-branch bandwidths of gaseous H₂ are shown in Supporting Information Figures S3 and S4. Under the same pressure conditions, the FWHMs of Q1 (0), Q1 (1), Q1 (2), and Q1 (3) slightly decreased as the temperature increased from 50°C to 400°C (except those for Q1 (0) at 30 and 40 MPa). These decreases were approximately 0.2 cm⁻¹ for Q1 (0), Q1 (2), and Q1 (3) and less than 0.1 cm⁻¹ for Q1 (1) (Supporting Information Figure S3). The pressure had a very significant effect on the FWHMs of the gaseous H₂ vibrational bands. For Q1 (0), Q1 (2), and Q1 (3), the bandwidth increases exceeded 0.8 cm⁻¹ as the pressure increased from 5 to 40 MPa, whereas for Q1 (1), the increase was approximately 0.3 cm⁻¹ (Supporting Information Figure S4).

Notably, except for the Q1 (0), the wavenumbers of the other three bands exhibited approximately the same behavior; that is, slowly increasing, or even decreasing (Q1 (1)), as the density increased under low temperature conditions (50–150°C) and quickly increasing under high temperature conditions (150–400°C; Figure 3). Generally, the temperature is thought to only weakly perturb vibrational motion; thus, the strong temperature dependence of hydrogen Raman wavenumbers is different from that of other gases (such as CO, N₂, and CH₄).[36–39,50] The relationship among the hydrogen peak position, the density, and temperature can be simply expressed with the following equation[38,44]:

$$\Delta Q_R = A\rho + B\rho^2,$$  \hspace{1cm} (1)

where $\Delta Q_R$ is the change in the Raman wavenumber as a function of the density in cm⁻¹; $\rho$ is the density of...
gaseous hydrogen in amagat, and A and B represent the line shift coefficients, which depend on the temperature, in cm\(^{-1}\) amagat\(^{-1}\) and cm\(^{-1}\) amagat\(^{-2}\), respectively.

The density of gaseous H\(_2\) reflects its molecular spacing, which can affect the intermolecular forces and Lennard–Jones potential. The temperature can influence the molecular distribution function, which determines the magnitude of the wavenumber perturbation.\(^{37-39}\) The temperature-dependent coefficients (A and B) of the Raman wavenumber are related to the population of the initial rotational level, isotropic intermolecular force, and vibrational coupling.\(^{51}\) The values of A and B for Q\(_1\) (J) (J = 0, 1, 2, and 3) in the temperature range of 100–400°C are shown in Supporting Information Table S1.

The trend of the bandwidth change with density shows three main characteristics (Supporting Information Figure S5). First, the bandwidth broadening has a positive correlation with the density of gaseous H\(_2\). Second, the temperature has a significant effect on the bandwidths of Q\(_1\) (0), Q\(_1\) (1), and Q\(_1\) (2) bands. At higher temperatures, the influence of the density on the bandwidth is more obvious. Third, the changes in the Q\(_1\) (3) bandwidth show a weak temperature dependence, and a linear relationship was obtained with the varying density. Three collisional mechanisms play significant roles in controlling the bandwidth as the density increases. Under low-density conditions, the collisional effect can be neglected, and the bandwidth is determined by Doppler broadening.\(^{52}\) As the pressure increases, the collision contribution to the bandwidth is more obvious. Dicke narrowing and collisional broadening play the dominant roles in the bandwidth changes as a function of the density in turn.\(^{53,54}\) In this study, under the conditions of 50–400°C and 5–40 MPa, only collisional broadening was observed in the bandwidth trend as the density varied. The increasing temperature can accelerate molecular thermal motion and the collision frequency, which will increase the relative number of perturbers of rotational state.\(^{44,53}\) According to the diffusion model, the relationship between the bandwidth and varying density in this study can be expressed by the simple equation:

\[
\Delta Q_{\text{FWHM}} = k_c^2 D_0 / \pi \rho + C \rho,
\]

where \(\Delta Q_{\text{FWHM}}\) is the change in the bandwidth as a function of the density in cm\(^{-1}\); \(k_c\) is the effective wave vector in cm\(^{-1}\); \(D_0\) is the self-diffusion coefficient in cm\(^{-2}\) amagat s\(^{-1}\); and C is the temperature dependence of the collision-broadening coefficient in cm\(^{-1}\) amagat\(^{-1}\).

Under high-density conditions, the self-diffusion width, \(k_c^2 D_0 / \pi \rho\), can be neglected. In this study, the bandwidth trend for Q-branch hydrogen as a function of the density can be linearly fitted. The temperature dependence of the collision-broadening coefficient (C) for Q\(_1\) (J) in the temperature range 100–400°C is shown in Supporting Information Table S2.
3.1.2 Dissolved H$_2$ in pure water and seawater

The peak positions and widths of the vibrational bands of dissolved H$_2$ in pure water and seawater are shown in Figure 4. Figure 4a shows that in pure water, the Raman wavenumbers of dissolved H$_2$ linearly decreased from 4,139 to 4,133 cm$^{-1}$ as the temperature increased from 50°C to 250°C whereas the rate of the decrease was reduced in the range of 250°C to 350°C. When the temperature was higher than 350°C, the change in the wavenumbers of dissolved H$_2$ with increasing temperature transformed from a decreasing trend to an increasing trend. Figure 4c shows that the pressure also affected the Raman peak of the dissolved H$_2$ slightly. From 50°C to 350°C, the wavenumbers of dissolved H$_2$ increased by approximately 0.5 cm$^{-1}$ as the pressure increased from 10 to 40 MPa. When the temperature was 400°C, the wavenumbers of dissolved H$_2$ decreased by approximately 1 cm$^{-1}$ with increasing pressure (20–40 MPa).

The effects of the temperature and pressure on the FWHM of dissolved H$_2$ were also investigated in this study. We found that the FWHMs of dissolved H$_2$ in pure water decreased by approximately 5 cm$^{-1}$ as the temperature increased from 50°C to 350°C, whereas the FWHMs increased by approximately 2 cm$^{-1}$ in the temperature range of 350–400°C (Figure 4b). We also found that when the temperature was lower than 350°C, the FWHMs of dissolved H$_2$ in pure water increased by approximately 1 cm$^{-1}$ as the pressure increased from 10 to 40 MPa and that when the temperature was 350°C to 400°C, the FWHMs decreased by approximately 1 cm$^{-1}$ as the pressure increased from 20 to 40 MPa (Figure 4d).

The changes in the vibrational spectra of dissolved H$_2$ in seawater were similar to those observed for dissolved H$_2$ in pure water. However, the wavenumbers and FWHMs of dissolved H$_2$ in seawater were approximately 0.5 cm$^{-1}$ lower and approximately 1 cm$^{-1}$ larger than that of dissolved H$_2$ in pure water, respectively.

In contrast to gaseous H$_2$, the vibrational band of dissolved H$_2$ showed a significant bandwidth broadening and a lower wavenumber shift (compared with that of Q$_1$ (1)), which reflected the interactions between the water molecules and hydrogen molecules, and these interactions were affected by the temperature and pressure (Figure 4). To the solvent effects, the redshift and blueshift are usually associated with attractive forces and repulsive forces, respectively. In Raman spectrum of dissolved H$_2$, the characteristics of the rotational structure have been completely erased, which indicates that the change of width is attributed to the vibrational relaxation. The combination of H$_2$ motion and H$_2$O motion gives rise to the vibrational relaxation for the solvent motion is slow compared with the vibrational time. The
weak influence of pressure to vibrational spectrum can be explained by the slight compression of water.\textsuperscript{[37,57]} When the temperature was above the critical temperature of water (374°C), the wavenumber and bandwidth trends were the opposite of those observed under lower temperature conditions (Figure 4a,b), which indicated that the interactions between the water molecules and hydrogen molecules were weakened with temperature increasing.

The formation of hydrogen bonds between water molecules causes electron redistribution, which increases the length of the O—H bond, while simultaneously shortening the bond distances of H—O and O—H.\textsuperscript{[58,59]} As the temperature increases, hydrogen bond fracturing can cause the distance between water molecules to increase, which also causes the distance between hydrogen molecules to increase.\textsuperscript{[58,60]} To prove the effects of hydrogen bonds to the combination, more research is needed. In addition, the increase of pressure can also strengthen the hydrogen bonds and decreases the O—O bond distance.\textsuperscript{[61,62]}

The differences in the spectra of dissolved H\textsubscript{2} in pure water and seawater can be ascribed to the effects of ions on the structure of water molecules. In aqueous seawater, water molecules form hydration shells around dissolved ions, which disturb the intermolecular hydrogen bond network. However, the effects of anion and cation on breaking water structure are still in debate.\textsuperscript{[63–66]}

### 3.2 Quantitative analysis of dissolved H\textsubscript{2} under high temperature, high pressure conditions

To quantitatively analyze the H\textsubscript{2} content in high temperature hydrothermal fluids, the relationship between the H\textsubscript{2} concentration and the intensity of the dissolved H\textsubscript{2} Raman vibrational peak was researched in this study. Although the relationship between the H\textsubscript{2}/H\textsubscript{2}O molar ratio and the partial pressure of hydrogen at normal temperatures has been studied by Borysow et al.\textsuperscript{[48]} and Ziparo et al.,\textsuperscript{[47]} experiments to establish a high temperature, quantitative Raman model for dissolved H\textsubscript{2} are still necessary. Raman spectroscopy can be used to quantify a component because the Raman signal intensity is proportional to the component concentration.

\[
R = IKP \sigma C, \tag{3}
\]

where \(R\) is the Raman signal intensity, \(I\) is the laser intensity, \(K\) represents the parameters of the instrument and samples, \(P\) is the optic path length, \(\sigma\) represents the Raman scattering cross section, and \(C\) is the concentration of the analyte.\textsuperscript{[67]}

However, it is difficult to calibrate the concentration of the analyte based on the absolute Raman signal intensity, because determining the values of \(I, K,\) and \(P\) is difficult and the value of \(\sigma\) can be affected by molecular interactions. According to the Placzek’s ratio method,\textsuperscript{[68,69]} for two Raman-active species \(a\) and \(b\) in a solution phase, their relative concentrations, \(C\)'s (e.g., mole or mol%), are proportional to their Raman peak areas, \(A\)'s, by the formula:

\[
A_a/A_b = (C_a/C_b)(\sigma_a/\sigma_b)(\eta_a/\eta_b) = (C_a/C_b)(F_a/F_b), \tag{4}
\]

where \(\eta\) and \(F\) are the instrumental efficiency and Raman quantification factor for peak area, respectively.

To the \(\text{H}_2–\text{H}_2\text{O}\) system researched in this study, the concentration of dissolved H\textsubscript{2} can be determined using the peak area ratio of \(A\) (H\textsubscript{2})/A (H\textsubscript{2}O). This approach has been successfully applied to analysis of the composition of fluid inclusion\textsuperscript{[69–73]} and to deep-sea in situ Raman detection.\textsuperscript{[67,74,75]} The \(\text{OH}\) bending mode band was chosen as an internal standard peak because it is relatively stable against temperature and pressure changes. In this study, the peak areas of dissolved H\textsubscript{2} and H\textsubscript{2}O were determined at 4,100–4,170 cm\textsuperscript{-1} and 1,450–1,830 cm\textsuperscript{-1}, respectively.

Gaseous H\textsubscript{2} and pure water were simultaneously pumped into the deep-sea extreme environment simulator. The dissolved H\textsubscript{2} concentration was determined based on the saturated solubility of H\textsubscript{2} in pure water; therefore, before collecting the dissolved H\textsubscript{2} Raman spectra, the H\textsubscript{2}–H\textsubscript{2}O system must be near the solubility equilibrium. The H\textsubscript{2}–H\textsubscript{2}O system was investigated at six temperatures (50°C, 100°C, 150°C, 200°C, 250°C, and 300°C) in the pressure range 0–40 MPa. In this study, the saturated solubilities of H\textsubscript{2} in pure water under the conditions of 50–300°C and 0–40 MPa were calculated using experimental data from Pray et al.\textsuperscript{[76]} and Baranenko and Kirov.\textsuperscript{[77]} Considering the possibility of finding hydrothermal fields more enriched in hydrogen in the future, the highest concentration of dissolved hydrogen used to establish quantitative model is about 0.69 mol/kg. Moreover, adding the high concentration data will reduce experimental error and improve the accuracy of the quantitative model. The values of peak area ratio of \(A\) (H\textsubscript{2})/A (H\textsubscript{2}O) and the corresponding hydrogen solubilities are tabulated in Supporting Information Table S3. The relationship between the peak area ratio of \(A\) (H\textsubscript{2})/A (H\textsubscript{2}O) and the dissolved H\textsubscript{2} concentration \(C\) (H\textsubscript{2}) in pure water is shown in Figure 5a. Two linear fitting lines were obtained with the following equations:

\[
A(\text{H}_2)/A(\text{H}_2\text{O}) = 1.437C(\text{H}_2) \quad (R^2 = 0.9851). \tag{5}
\]
In these equations, the concentrations of dissolved H$_2$ ($C$ (H$_2$)) were expressed in molality (mol/kg). The difference between these two fitting lines arose from the discrepancy in the experimental solubility data. In the ranges of 50–300°C and 0–40 MPa, the peak area ratio of $A$ (H$_2$)/$A$ ($H_2O$) linearly increased as the H$_2$ concentration increased. In our investigated hydrogen concentration range (0–0.69 mol/kg), the effects of the dissolved H$_2$ concentration on both the Raman spectral characteristics of H$_2$ and the linearity of the quantitative model were not observed. The data collected under high temperature conditions were not separated from that collected under low temperature conditions, which indicated that the calibration model for dissolved H$_2$ can be applied to higher temperature and pressure conditions.

The limit of detection (LOD) and limit of quantitation (LOQ) for the dissolved H$_2$ calibration model were determined at 100°C. The pressure of the simulation system was controlled at 0.3, 0.4, and 0.5 MPa, which correspond to H$_2$ concentrations of 1.3, 2.0, and 2.8 mmol/kg, respectively. When the pressure was above 0.3 MPa (1.3 mmol/kg), the H$_2$ peak intensity was approximately 3 times higher than the noise. When the pressure was above 0.5 MPa (2.8 mmol/kg), the H$_2$ peak intensity was approximately 10 times higher than the noise. Therefore, the H$_2$ LOD and LOQ of the RiP system were approximately 1.3 and 2.8 mmol/kg, respectively (Figure 5b). Both the LOD and LOQ for dissolved H$_2$ will be improved with the upgrade of the RiP system.

In this study, the relationship between the H$_2$ concentration and the Raman vibrational peak intensity of dissolved H$_2$ in seawater or a salt water environment was not investigated for the lack of a high temperature solubility model for H$_2$ in seawater or salt water. Based on our quantitative analysis experience and previous studies, the quantitative analysis model in pure water is also suitable for low ion content solutions, such as seawater.[78,79]

4 | CONCLUSION

In this study, we researched the characteristics of gaseous H$_2$ and dissolved H$_2$ vibrational spectra in pure water under conditions up to 400°C and 40 MPa. The hydrogen molecular interactions and their molecular distribution are the main contributors to the peak position shift and bandwidth change of gaseous H$_2$. The interactions between the water molecules and hydrogen molecules result in changes in the dissolved H$_2$ vibrational band as a function of temperature and pressure. The discrepancy between the dissolved H$_2$ vibrational band in pure water and seawater is ascribed to the effects of ions on the structure of water molecules. The relationships between the dissolved H$_2$ content and the dissolved H$_2$ vibrational band intensity were fitted with linear equations. Under high temperature conditions, the peak area ratio of $A$ (H$_2$)/$A$ ($H_2O$) linearly increases with the H$_2$ concentration, indicating that the calibration model can be applied to higher temperature and pressure environments. Although the method of in situ Raman detection for H$_2$ can be applied only in high H$_2$ environments at present, it shines some light on the direct approach to determine the concentration of dissolved H$_2$ in high temperature hydrothermal fluids. The detection ability for H$_2$ will also be improved with the upgrade of the RiP system.
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ORCID

Xin Zhang http://orcid.org/0000-0003-4898-5956

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