Raman spectroscopic quantification of sulfur species in aqueous solutions

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Raman spectroscopy can be applied to determine the speciation of sulfur in aqueous solutions, even in *in situ* studies at the pressure-temperature conditions of the Earth's crust and subduction zone environments. This requires knowledge of relative scattering cross sections of Raman bands of sulfur species and water. Most such information in the literature is on oxidized sulfur species and often presented in a form that is not or only with difficulty, applicable to other instrumental and analytic conditions. Very little information can be found on relative cross sections or intensities of Raman bands of the reduced species, H_2S(aq), which is ubiquitous in ore-forming and other geological fluids, HS^-(aq), and of S_3^-(aq) and other polysulfides. From spectra acquired at 22 °C and 0.1 MPa, we determined ratios of the relative molar scattering factors for the Raman bands of H_2S(aq) at ~2590 cm^{-1}, HS^-(aq) at ~2570 cm^{-1}, SO_2(aq) at ~1150 cm^{-1}, HSO_4^-(aq) at ~1050 cm^{-1}, $S_2O_3^{2-}$(aq) at ~445 cm^{-1}, the bending mode of H_2O at ~1640 cm^{-1} and the O–H stretching band of water at ~3400 cm^{-1} to the relative molar scattering factor for the Raman band of SO_4^{2-}(aq) at ~980 cm^{-1}. Furthermore, we estimated this ratio for the Raman band of S_3^-(aq) at ~535 cm^{-1} from spectra collected in experiments up to 600 °C and 1.36 GPa using a hydrothermal diamond-anvil cell [1]. The ratios were obtained for excitation at wavelengths of 473 and 532 nm. To facilitate applicability in other laboratories, the ratios were based on spectra corrected for the response function of the spectrometer, the frequency and scattering factor, and the Bose-Einstein factor plus one, in addition to the normalizations to the density of the fluid, accumulation time and laser power [2]. The diamond-anvil cell experiments on a 1.13 molal H_2SO_4 solution also suggested a significant decrease in the Raman scattering cross section of the band of HSO_4^-(aq) at ~1050 cm^{-1} with temperature at elevated pressure. The new Raman spectroscopic data together with available thermodynamic data permit a rigorous evaluation of hydrothermal sulfur species stabilities.

[1] Bassett *et al*. (1993) *Rev. Sci. Instr*. **64**, 2340. [2] Schmidt (2009) *Geochim. Cosmochim. Acta* **73**, 425.