

## Raman spectroscopic experiments on sulfur in hydrothermal fluids

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Raman spectroscopy has been applied for several decades to determine and quantify sulfur species in minerals, melts and hydrothermal fluids. It has become an indispensable tool in studies of inclusions and in experiments using optical cells, which permit analyses of fluids in situ at high temperature and pressure. Such studies have shown a wealth of information, for example on redox state and pH of fluids, partitioning of sulfur species between aqueous fluid and silicate melt, changes in sulfur speciation with pressure and temperature, structural changes in the solvent water, and the discovery of pressure-induced ion pairing in cold H<sub>2</sub>O-MgSO<sub>4</sub> solutions, which is relevant for studies of subsurface oceans in extraterrestrial planetary bodies.

The availability of robust, laboratory-independent, methods to quantify dissolved sulfur species concentrations from Raman spectra is of central importance for applications in hydrothermal geochemistry, and Terry Seward contributed significantly to their development (Schmidt and Seward 2017). This non-trivial task requires fundamental spectroscopic information such as on absorption corrections and on the changes in scattering efficiencies of Raman active species with pressure and temperature. Yet, open questions remain, for example on the cause of the asymmetric shape of the  $\nu_s(\text{SO}_3)$  Raman band of HSO<sub>4</sub><sup>-</sup>(aq), or on the cause of the unusually strong decrease in the Raman scattering efficiency of this band observed by Schmidt and Seward (2017) upon heating a 1.13 molal H<sub>2</sub>SO<sub>4</sub> solution. We studied the Raman spectra of NaHSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> solutions to 1000 K, experimentally and by ab initio molecular dynamics simulation, and found very different behavior (see Figure). The results indicate that the scattering efficiencies of the  $\nu_s(\text{SO}_3)$ ,  $\nu_{\text{as}}(\text{SO}_3)$ , and  $\nu_s(\text{S-OH})$  Raman bands of HSO<sub>4</sub><sup>-</sup>(aq) depend on pH. We attribute this and the asymmetric shape of this band to proton mobility in the HOSO<sub>3</sub><sup>-</sup> molecule.

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Figure: Sulfur speciation in initially 7.6 molal NaHSO<sub>4</sub> and 4.34 molal H<sub>2</sub>SO<sub>4</sub> solutions calculated from corrected integrated intensities of Raman bands (for HSO<sub>4</sub><sup>-</sup> from  $\nu_s(\text{SO}_3)$ ) plotted as function of temperature. Sulfur in the vapor phase is not taken into account. P<sub>v</sub> – vapor pressure.

