

## **New Raman constraints on the bisulfite isomer quotient: Implications for isotope fractionations in aqueous systems**

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Bisulfite ( $\text{HSO}_3^-$ ) compounds play key roles in numerous (bio)geochemical processes extending from the atmosphere to the seafloor biosphere. In organic-rich seafloor sediments, bisulfite and sulfite ( $\text{SO}_3^{2-}$ ) form as intermediates between intracellular enzymatic transformations in dissimilatory sulfate reduction, a major anaerobic pathway in the global respiration budget [1], which influences the overall sulfur [2] and oxygen [3] isotope fractionations associated with this metabolism. Results of recent theoretical calculations [4] illustrate the potential for complex equilibrium sulfur isotope fractionations among aqueous bisulfite/sulfite compounds because bisulfite exists in two isomeric forms that differ structurally in the placement of the proton (one H-O bonded, one H-S bonded). The H-S bonded isomer, which occurs in minor abundance, is expected to influence nearly all aspects of bulk sulfite/bisulfite fractionation behavior in aqueous solution (i.e.,  $1000\ln(^{34}\alpha) \approx 20\text{-}22\text{‰}$  between HS-bisulfite and HO-bisulfite/sulfite at  $25^\circ\text{C}$  [4]). Despite decades of spectroscopic investigations, the molecular composition of  $\text{HSO}_3^-$  in solution remains uncertain and, thus, the role of bisulfite in isotope fractionation processes is unclear. We provide updated estimates of the bisulfite isomer quotient ( $Q_i = [(\text{HO})\text{SO}_2]/[(\text{HS})\text{O}_3^-]$ , [ ] = concentration) in aqueous solution as a function of temperature ( $5\text{-}85^\circ\text{C}$ ) by using Raman spectroscopy. Preliminary data seem to indicate that the minor H-S bonded isomer may be more abundant in low ionic strength solutions than is suggested by previous Raman [5] and high ionic strength  $^{17}\text{O}$ -NMR [6] determinations. The H-S bonded isomer may comprise between  $\sim 24\%$  to  $\sim 37\%$  of  $\text{HSO}_3^-$  from  $5$  to  $85^\circ\text{C}$ , respectively. These new experimental data combined with published [4] and recent theoretical calculations of compound specific equilibrium fractionation factors among bisulfite/sulfite compounds have been employed to re-assess the sulfur and oxygen isotope mass balance of sulfite/bisulfite solutions, and their implications for fractionations expressed by microbial metabolism.

[1] Bowles et al. (2014) *Science* **334** 889-891; [2] Wing and Halevy (2014) *PNAS* **111** 18116-18125; [3] Wankel et al. (2013) *GCA* **125** 694-711; [4] Eldridge et al. (2016) *GCA* **195** 171-200; [5] Littlejohn et al. (1992) *Appl. Spect.* **46** 848-851; [6] Horner and Connick (1986) *Inorg. Chem.* **25** 2414-2417.