

## Mode-projected vibrational analysis and Raman spectra of silica species in aqueous solution using *ab initio* molecular dynamics

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In this study, we investigate the vibrational properties of silica species in aqueous solution to understand their contributions to Raman spectra. This is important, *e.g.* in geosciences or zeolite research, for understanding the structure and properties of silica-bearing fluids. Investigated species include  $\text{H}_4\text{SiO}_4$  and  $\text{H}_3\text{SiO}_4^-$  monomers,  $\text{H}_6\text{Si}_2\text{O}_7$  and  $\text{H}_5\text{Si}_2\text{O}_7^-$  dimers and higher polymers. However, assignment of Raman bands to specific silica species is still often debated (*e.g.* Zotov 2000, Tossell 2005).

We model these species using *ab initio* molecular dynamics with periodic boundary conditions in the environment of 25-27  $\text{H}_2\text{O}$  molecules at 1000 K and fluid density around  $1 \text{ g/cm}^3$ . The concept of mode-projected velocity autocorrelation (VACF) and its Fourier transform (Taraskin and Elliott 1998, Pavlatou *et al.* 1997) is applied to yield normal-mode-like vibrational sub-spectra of the vibrational density of states, *e.g.* from tetrahedral subunits or Si-O-Si units of bridging oxygens. We extend this method to other subunits such as the ammonia-like  $\text{Q}^1$  and its normal-mode-like vibrations. Since *ab initio* calculations at the level used here (PBE as exchange-correlation functional) systematically underestimate vibrational frequencies, we apply a correction factor of 1.055 to match experimental frequencies.

For the  $\text{H}_4\text{SiO}_4$  monomer, we observe the symmetric stretch vibration at  $\sim 770 \text{ cm}^{-1}$  as the only sharp contribution. For the  $\text{H}_3\text{SiO}_4^-$  deprotonated monomer, this vibration is even stronger relative to all other the tetrahedral normal-mode-like vibrations.

For the  $\text{H}_6\text{Si}_2\text{O}_7$  dimer, the strongest and sharpest contribution results from the inter-tetrahedral symmetric stretch at  $\sim 885 \text{ cm}^{-1}$ . This frequency is in agreement with *ab initio* gas-phase calculations (Tossell, 2005). The individual  $\text{NH}_3$ -like symmetric stretch of the two  $\text{Q}^1$ -tetrahedra lies at  $\sim 822 \text{ cm}^{-1}$ , the individual  $\text{NH}_3$ -like asymmetric stretch lies at  $\sim 960 \text{ cm}^{-1}$ . A band around  $1000\text{-}1100 \text{ cm}^{-1}$  is caused by the bridging-oxygen Si-O-Si asymmetric stretch. Other modes, also on higher polymers, will be presented and compared to experimentally obtained Raman spectra of Na-Si-O-H fluids.

Although the calculations can be executed on a commodity cluster, the computational demand limits the sampling time such that peak positions and peak widths are subject to some statistical error. However, the combination of *ab initio* molecular dynamics and the mode-projected VACF has the following advantages: 1) it records vibrations “*in-situ*” under defined pressure, temperature, composition and *pH*, 2) it does not use the harmonic approximation, nor does it put geometrical constraints on the molecules, 3) it yields frequencies that are explicitly linked to specific molecular vibrations, and 4) it allows investigation of silica species with any degree of polymerization.

### References:

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