

## Ab initio calculation method as a practical mean for predicting $^{17}\text{O}$ and $^{29}\text{Si}$ NMR properties of silicates

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Ab initio molecular orbital calculations have been carried out for silica polymorphs coesite, cristobalite and quartz, in order to investigate the reliability of this method for predicting  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR properties (chemical shifts and electric field gradient-related parameters) of silicates. O- and Si- centered clusters consisting of one to three tetrahedral shells (one to four atomic shells), taken from real crystal structure, have been investigated. It is found that that both the  $^{29}\text{Si}$  and  $^{17}\text{O}$  chemical shifts have reached convergence with cluster size at the OH-terminated two tetrahedral shell (3 atomic shell) model. Our study suggests that the ab initio calculation method is a reliable mean for predicting  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR parameters for silicates.

Ab initio molecular orbital calculations (Hartree-Fock and density functional theories) have been carried out for silica polymorphs coesite, cristobalite and quartz, in order to investigate the reliability of this method for predicting  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR properties (chemical shifts and electric field gradient-related parameters) of silicates. O- and Si- centered clusters consisting of one to three tetrahedral shells (one to four atomic shells), taken from real crystal structure, have been investigated. It is found that that both the  $^{29}\text{Si}$  and  $^{17}\text{O}$  chemical shifts have reached convergence with cluster size at the OH-terminated two tetrahedral shell (3 atomic shell) model. At convergence, the calculated  $^{29}\text{Si}$  chemical shift values agree well (within 1 ppm) with experimental data; The calculated  $^{17}\text{O}$  electric field gradient- related parameters also agree well with experimental data (within experimental uncertainties). The calculation also reproduces well small differences in  $^{17}\text{O}$  chemical shifts for O sites with similar local structures, but shows deviations up to about 10 ppm in relative difference for O sites with different tetrahedral connectivities. The poor performance for the latter is mainly due the approximations of the Hartree-Fock method, which might be improved by employing density functional theory using magnetic field dependent current functionals. Our study thus suggests that the ab initio calculation method is a reliable mean for predicting  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR parameters for silicates. Such an approach should find application not only to well-ordered crystalline phases, but also to disordered materials, by combining with other techniques, such as the molecular dynamics simulation.