Hydrogen bonds and vibrations of water on (110) rutile

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We study the relation between hydrogen bonding and the vibrational frequency spectra of water on the (110) surface of rutile (α-TiO_2) with three structural layers of adsorbed water. Using *ab-initio* molecular dynamics simulations at 280, 300 and 320K, we find strong, crystallographically-controlled adsorption sites, in general agreement with synchrotron X-ray and classical MD simulations. We demonstrate that these sites are produced by strong H-bonds formed between the surface oxygen atoms and sorbed water molecules. The strength of these bonds is manifested by substantial broadening of the stretching mode vibrational band. The overall vibrational spectrum obtained from our simulations is in good agreement with inelastic neutron scattering experiments. We correlate the vibrational spectrum with different bonds at the surface in order to transform these vibrational measurements into a spectroscopy of surface interactions.

The stretching band of the vibrational spectrum of water molecules and OH groups is particularly sensitive to hydrogen bonding. In this heterogeneous interface, there is a large variety of hydrogen bonds between the surface species and water and among the water molecules at the surface. Each of these types has different characteristic hydrogen bond strength and, consequently, a characteristic contribution to the stretching mode band of the associated water molecules or hydroxyls. Inelastic neutron scattering measurements of water confined at the surface of the anatase polymorph of TiO_2 showed a surprising softening of this band, extending to frequencies as low as 85 THz (350 meV), [27] which we also observe in the VDOS extracted from our simulations. We provide evidence that the softening is produced by strong hydrogen bonding between surface species and the hydration layer. We identified two very strong hydrogen bonds between the atoms at the surface and the water molecules in the hydration layer. These two bonds dominate the contributions to the VDOS in the lower end of the OH stretching band.

Microgranular enclaves in Ladakh batholith, NW Indian Himalaya: Implication on magma chamber processes in subduction setting

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Felsic and associated magmatic rocks (102-48 Ma) [1] constitute the Ladakh batholith (trending NW-SE, *ca* 30,000 km^2) in northwest Indian Higher Himalaya bounded by Shyok Suture Zone in the north and Indus Tsangpo Suture Zone in the south [2], which represent an integral part of Trans-Himalayan calc-alkaline, Andean type magmatic arc. Ladakh granitoids (LG) are largely characterized as calc-alkaline, magnetite to ilmenite series granitoids, and contain coeval mafic, hybrid and composite microgranular enclaves (ME) [3], mafic schlieren and dykes. Mineralogy and geochemistry of ME and host LG have been carried out in order to understand magma chamber processes in subduction setting. ME are rounded to elongate having sharp, crenulate, and diffuse contacts with felsic host, and size varies from cms to metres across. Biotites of ME and LG exhibit bimodal $2Al \rightleftharpoons 3Fe^{2+}$ and $Mg \rightleftharpoons Fe$ substitutions typically formed in peraluminous (S-type) and metaluminous (I-type) felsic melts respectively. Al-in-hornblende barometer suggests emplacement of northwest LG at P=2.5-3.5 kbar, central LG at P=3-4 kbar and southeastern LG at P=3.5 kbar, which point to differential unroofing of magma chamber(s). Most ME globules appear undercooled at LG levels but some small ME are frozen enroute at ca P=5.0 kbar. Near linear trends for TiO_2, CaO, $Fe_2O_3^t$, MgO, against SiO_2 of ME-LG can be attributed to mafic-felsic magma mixing whereas scatter for Al_2O_3, alkalies, MnO, P_2O_5, Rb and Ba appears caused by diffusion during syn-crystallization and modal mineral variations. Parallel to subparallel REE patterns with negative Eu-anomalies of LG-ME may be attributed to differential degrees of chemical equilibration. Several lines of evidences suggest that Ladakh batholith truly represents composite mafic-silicic intrusive (MASLI) system [4], and ME in LG are mafic and mixed products of mantle- and slab-derived magmas concomitant fractional differentiation, mingling, and diffusion mechanisms.

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