

MOLECULE-MINERAL INNER SURFACE INTERACTIONS IN NANOPOROUS SILICATES: A RAMAN SPECTROSCOPIC INVESTIGATION

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We have undertaken single-crystal Raman measurements of zeolites (bikitaite, natrolite), SiO₂-clathrates (melanophlogite) and other silicate structure types with small nanopores (beryl, cordierite, hemimorphite) at different temperatures. The goal is to investigate the nature of inner surface molecule-crystal interactions and the role of hydrogen bonding in minerals. The angular dependencies of the OH-mode scattering intensities in single-crystal measurements, made at low and ambient temperatures, permit the direction of the molecular bonds and the main molecular polarizabilities for different O-H bonds to be obtained.

In bikitaite, H₂O molecules occur in infinite [010] channel ways and build a hydrogen-bonded H₂O chain termed 'one-dimensional ice'. The molecules are ordered, whereby one H atom per molecule is unbonded and the other is hydrogen-bonded to a neighboring H₂O molecule. They show little interaction with the framework. The hydrogen-bonded O-H stretching bands in the Raman spectra show little line broadening, which is not typical for many hydrogen-bonded systems. With increasing temperature, the hydrogen bonding weakens continuously until the chain 'breaks' and isolated H₂O molecules are present.

The Raman spectrum of melanophlogite shows the presence of quasi-free N₂, CO₂ and CH₄, but no H₂O molecules. Most of the CH₄ is partitioned into the smaller nearly spherical [5¹²] cage, while CO₂ and N₂ appear to prefer the larger more oblate [5¹²6²] cage. The difference in wavenumber for their stretching modes between room temperature and 4 K is minimal. The molecules are orientationally disordered in the cavities and they have only weak dispersion interactions with the SiO₂-crystal framework. However the incorporation of molecules is necessary to allow the SiO₂ framework to condense.

Cordierite and beryl contain quasi-free CO₂ molecules, as well as H₂O in small cavities. The CO₂ molecules are orientated parallel to the crystallographic *x*-axis. The H₂O molecules have their H-H vector parallel to the *z*-axis in alkali-free crystals and are dynamically disordered about the *z*-axis. They show little hydrogen bonding with their frameworks.

It is noteworthy that the polar H₂O molecule can be found in these two 'zeolite-like phases', but not in melanophlogite. Melanophlogite is hydrophobic, while nearly all other nanoporous silicates are hydrophilic. The incorporation of the polar H₂O molecule may be related to the nature of the electronic charge distribution within the crystal framework.