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Behavior of H_2O molecules in the channels of natrolite and scolecite: A Raman and IR spectroscopic investigation of hydrous microporous silicates

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ABSTRACT

Single-crystal polarized Raman spectra (80 to 4000 cm^{-1} at $4 \leq T \leq 700$ K) and powder IR spectra (1500 to 4000 cm^{-1} at $50 < T < 300$ K) were measured for two microporous zeolites natrolite, $Na_{16}[Al_{16}Si_{24}O_{80}]\cdot 16H_2O$, and scolecite, $Ca_8[Al_{16}Si_{24}O_{80}]\cdot 24H_2O$ to determine the behavior of H_2O molecules in the channels. Both IR and Raman spectra show intense O-H stretching and H_2O bending modes derived from the hydrogen-bonded H_2O molecule(s) in the channels. Using published crystal structural data for natrolite and scolecite, and a consideration of Raman mode intensities that are sensitive to the H_2O orientation in the framework channels, the internal stretching and bending modes could be assigned. The Raman spectra also show lower energy lattice modes and, in addition, second-order scattering in the wavenumber range where O-H stretching vibrations occur. The stretching vibrations of H_2O molecules of natrolite and scolecite are located between 3200 and 3700 cm^{-1} and bending vibrations occur around 1650 cm^{-1}. In the case of natrolite, two intense O-H stretching modes can be observed and also several weaker combination modes. The latter was used to derive a low energy external H_2O translational vibration, $T(H_2O)$, which is also observed directly in single-crystal Raman spectra. In addition, two H_2O librational modes are located at about 440 and 500 cm^{-1}. For scolecite, six O-H stretching modes are observed in the Raman spectra recorded at 4 K, but only five are found at room temperature in the IR or Raman. The single-crystal Raman spectra also show several second-order combination modes consisting of external and internal H_2O vibrations. They permit the wavenumber of several $T(H_2O)$ modes at low wavenumbers to be determined. These combination bands are analyzed based on their temperature behavior between 0 and 300 K. It is shown that the wavenumber of the H_2O bending modes decreases with an increase of the H-O-H angle of the H_2O molecule in natrolite and scolecite. The dehydration behavior of H_2O in natrolite and scolecite was investigated by Raman measurements of the intensities of the O-H stretching modes at temperatures from 300 K to 570 K and 720 K, respectively. IR and Raman spectra, obtained over a large temperature range, permit one to obtain a better understanding of inner surface H_2O-molecule behavior in microporous silicates and energetics and the behavior of hydrogen bonding.

Keywords: Raman spectroscopy, IR spectroscopy, natrolite, scolecite, microporous materials, Hydrogen bonding, zeolites, H_2O molecules