Behavior of H\textsubscript{2}O molecules in the channels of natrolite and scolecite: A Raman and IR spectroscopic investigation of hydrous microporous silicates

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\textbf{ABSTRACT}

Single-crystal polarized Raman spectra (80 to 4000 cm\textsuperscript{-1} at 4 ≤ T ≤ 700 K) and powder IR spectra (1500 to 4000 cm\textsuperscript{-1} at 50 < T < 300 K) were measured for two microporous zeolites natrolite, Na\textsubscript{16}[Al\textsubscript{16}Si\textsubscript{24}O\textsubscript{80}]\textsubscript{·16H\textsubscript{2}O, and scolecite, Ca\textsubscript{8}[Al\textsubscript{16}Si\textsubscript{24}O\textsubscript{80}]\textsubscript{·24H\textsubscript{2}O to determine the behavior of H\textsubscript{2}O molecules in the channels. Both IR and Raman spectra show intense O-H stretching and H\textsubscript{2}O bending modes derived from the hydrogen-bonded H\textsubscript{2}O 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\textsubscript{2}O 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\textsubscript{2}O molecules of natrolite and scolecite are located between 3200 and 3700 cm\textsuperscript{-1} and bending vibrations occur around 1650 cm\textsuperscript{-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\textsubscript{2}O translational vibration, T(H\textsubscript{2}O), which is also observed directly in single-crystal Raman spectra. In addition, two H\textsubscript{2}O librational modes are located at about 440 and 500 cm\textsuperscript{-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\textsubscript{2}O vibrations. They permit the wavenumber of several T(H\textsubscript{2}O) 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\textsubscript{2}O bending modes decreases with an increase of the H-O-H angle of the H\textsubscript{2}O molecule in natrolite and scolecite. The dehydration behavior of H\textsubscript{2}O 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\textsubscript{2}O-molecule behavior in microporous silicates and energetics and the behavior of hydrogen bonding.

\textbf{Keywords:} Raman spectroscopy, IR spectroscopy, natrolite, scolecite, microporous materials, Hydrogen bonding, zeolites, H\textsubscript{2}O molecules

\textbf{INTRODUCTION}

Zeolites are used in several technological applications and also comprise an important rock-forming mineral group. Zeolites are used as catalysts, for example, in the cracking of hydrocarbons, in molecular sieving and for use in cation-exchange processes. In nature, they can be found in sedimentary rocks, in low-grade metamorphic assemblages and in various hydrothermal deposits. The chemistry of zeolites with a single cation in the channels (we use here the terminology based on the IUPAC recommendations outlined by Mc Crusker et al. 2001) can be represented by the general formula M\textsubscript{n}[Al\textsubscript{2}O\textsubscript{4}](SiO\textsubscript{2})\textsubscript{m}·H\textsubscript{2}O, where M is a cation of valence n and m is the number of water molecules in the unit cell (Gottardi and Galli 1985). In terms of their crystal structures zeolites are classified as framework silicates consisting of corner-linked AlO\textsubscript{4} and SiO\textsubscript{4} tetrahedra. To balance the negative charge in the framework, resulting from the presence of the Al cations, M cations are located in structural channels. The M cation is typically monovalent such as Li\textsuperscript{+} and Na\textsuperscript{+}, or divalent such as Mg\textsuperscript{2+} or Ca\textsuperscript{2+}, for example. H\textsubscript{2}O molecules are also found in the structural channels and are present in different concentrations. H\textsubscript{2}O can be easily driven out of the channels by heating zeolites at relatively low temperatures (Cronstedt 1756). Thus, one can readily understand his derivation of the word zeolite, which from the Greek means boiling stone. Smith (1963) offered an early definition as: “a zeolite is an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration.”

Herein, we focus on the behavior of the H\textsubscript{2}O molecules located in the two fibrous zeolites natrolite, Na\textsubscript{16}[Al\textsubscript{16}Si\textsubscript{24}O\textsubscript{80}]\textsubscript{·16H\textsubscript{2}O, and scolecite, Ca\textsubscript{8}[Al\textsubscript{16}Si\textsubscript{24}O\textsubscript{80}]\textsubscript{·24H\textsubscript{2}O. Both natrolite and scolecite can be classified as small-pore zeolites consisting of eight-membered rings having channels around 2.5 × 4 Å in size that are parallel to the crystallographic c-axis. Surprisingly, inasmuch as...