Raman investigation of H$_2$O molecule and hydroxyl groups in the channels of hemimorphite

BORIS KOLESOV*

Institute of Inorganic Chemistry, Russian Academy of Sciences, Lavrentiev av. 3, Novosibirsk 630090, Russia

ABSTRACT

Single-crystal polarized Raman spectra (40 to 4000 cm$^{-1}$ at 4 $\leq T \leq$ 860 K) were measured for hemimorphite, Zn$_4$Si$_2$O$_7$(OH)$_2$H$_2$O, to determine the behavior of H$_2$O molecules and OH groups in the channels. All observed stretching modes of the O-H vibrations could be assigned. Low-temperature Raman spectra show the presence of two different spatially divided regions in the crystal where the H$_2$O molecules and hydroxyl groups have slightly different positions in the channel. Two structural phase transitions were observed at 20–30 and 80–100 K, respectively, which reflect temperature replacement and reorientation of the H$_2$O molecules in the cavity. At $T >$ 100 K, H$_2$O molecules are rotationally disordered around the $c$ axis. An analysis of combined modes consisting of external and internal H$_2$O vibrations permits the frequency of translational T(H$_2$O) modes at 30, 53, 71, 90, 118, and 148 cm$^{-1}$ to be determined. The T(H$_2$O) modes also can be observed directly at low frequencies in the Raman spectra. The dehydration process of hemimorphite was investigated by Raman measurements at elevated temperatures of the crystal. One of two hydroxyl groups in the dehydrated crystal is hydrogen-bonded to neighbor oxygen and disordered statistically.

Keywords: Hemimorphite, H$_2$O molecules, microporous minerals, Raman spectroscopy

INTRODUCTION

There is considerable interest at the present time in understanding the nature of molecular fluids in various environmental and low-temperature geological systems. Surface reactions on minerals and rocks, and mineral weathering and dissolution are examples of the types of low-temperature geological processes that are controlled principally by the behavior of H$_2$O-rich fluids and their interaction with solid Earth materials.

However, the nature of local molecule-mineral interactions is so complex that an interpretation of many experimental data, and even more importantly obtaining quantitative physical understanding, is often difficult if not impossible. Thus, it is necessary to investigate “simple systems” to establish some physical scientific basis before more complicated systems can be investigated. It is here that studies of the H$_2$O molecule in micro and nanoporous minerals and inner-surface-type interactions can be extremely useful. This is because either a single or a small number of H$_2$O molecules are contained in the micro and nanopores of a crystalline structure, often in a structurally ordered way. As a result, it is easier to understand the nature of their molecule-mineral interactions compared to those occurring on outer surfaces and that are highly disordered.

Hemimorphite, Zn$_4$Si$_2$O$_7$(OH)$_2$H$_2$O, is a low-temperature phase typically found in oxidized zones of zinc ore deposits. The hemimorphite crystal structure is characterized by relatively small cavities that contain single H$_2$O molecules (McDonald and Cruickshank 1967 and reference therein). The molecules lie in the (010) plane with their rotation axes parallel to [001]. Within the cavities, the H$_2$O molecules are hydrogen bonded to two O atoms as a donor of hydrogen bonds, i.e., acid, and two H atoms as an acceptor of hydrogen bonds, i.e., base, both of which are part of the framework (Fig. 1b). Thus, all the donor and acceptor sites of the H$_2$O molecule are bonded (Hill et al. 1977; Takeuchi et al. 1978). From this point of view, the arrangement of the water molecule in hemimorphite at room temperature could be described as “two-dimensional ice” because all four hydrogen bonds of the H$_2$O in the cavity are coplanar. The hydrogen bonds between the H$_2$O molecule and the framework O atoms (O3 atoms) are weaker than those between the H$_2$O molecule and the OH groups (H3 atoms). It confirms the well-known rule that the water is a strong acceptor and a relatively weak donor of hydrogen bonds (Jeffrey 1997, p. 59). At low temperature, the water molecule is displaced from the center of the cavity to the side of the a-c plane (Libowitzky et al. 1998). Only two relatively strong bonds remain in the water molecule: one donor hydrogen bond with O3 atom and one acceptor hydrogen bond with hydroxyl group (Fig. 1a). Upon heating hemimorphite at 1 atm, H$_2$O loss occurs in two stages (Faust 1951; Taylor 1962): molecular H$_2$O starts to be expelled around 570 K and is completely gone around 770 K. During dehydration, the structural framework undergoes only minor adjustments. In the second stage, dehydration occurs at about 930 K and, ultimately, a reconstructive transformation to the anhydrous phase $\beta$-Zn$_2$SiO$_4$ occurs (Taylor 1962).

At room temperature, hemimorphite is orthorhombic, space group Imm2 with $Z = 2$ (McDonald and Cruickshank 1967). The zone center vibrations at the Γ point are described by irreducible representation:

\[ \Gamma = 14 A_1 + 10 A_2 + 12 B_1 + 12 B_2 \]

* E-mail: kolesov@che.nsk.su