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Raman spectroscopic study of H_2O in bikitaite: "One-dimensional ice"

BORIS A. KOLESOV[1] **AND CHARLES A. GEIGER**[2,*]

[1]Institute of Inorganic Chemistry, Lavrentiev prosp. 3, Novosibirsk 630090, Russia
[2]Institut für Geowissenschaften, Universität Kiel, Olshausenstr. 40, 24098 Kiel, Germany

ABSTRACT

The zeolite bikitaite, $Li_2[Al_2Si_4O_{12}]\cdot 2H_2O$, has structural channels containing infinite chains of H_2O molecules running parallel to [010]. One hydrogen atom of an H_2O molecule is weakly hydrogen bonded to an O atom of a neighboring molecule, while the other hydrogen atom is unbonded. The molecules are ordered and the chains they form have been called "one-dimensional ice." Polarized Raman spectra of single crystals in the wavenumber range 40–4000 cm^{-1} were measured from 5 to 625 K. At low temperatures, four different O-H stretching vibrations can be observed between 3330 and 3600 cm^{-1}, as well as H_2O bending vibrations at about 1640–1650 cm^{-1}. The two lower wavenumber hydrogen-bonded O-H stretching modes increase in wavenumber with increasing temperature, while the higher wavenumber non-hydrogen-bonded OH modes decrease in wavenumber. The temperature dependence of the linewidths of the O-H stretching modes and the degree of hydrogen bonding between neighboring H_2O molecules show that the main cause of line broadening is modulation of the OH potential from low-energy thermal O···O vibrations in the H_2O chains. At elevated temperatures, the different O-H stretching modes become similar in energy and only a single symmetric H_2O stretching band is observed above 520 K. At these temperatures the H_2O molecules lose their hydrogen bonding and are only bonded to Li cations at the walls of the channels.

INTRODUCTION

Certain minerals contain molecules in channels or cavities of varying shapes and sizes. These structural voids are able to trap and exchange extra framework molecules. Such structures are of interest from a catalysis and selective sorption point of view. The incorporation of H_2O molecules into cavities, and the formation of hydrogen bonds, presents an excellent opportunity to study this type of bonding. This is because the crystal framework provides a "matrix" for ordered hydrogen-bonded molecules that can be investigated over a wide temperature range as compared to, for example, molecules in gas matrices, gases, solutions, or even to H_2O in ice.

One such mineral is the zeolite bikitaite, $Li_2[Al_2Si_4O_{12}]\cdot 2H_2O$, which contains two H_2O molecules per unit cell. It has a framework structure consisting of chains of corner-sharing SiO_4 and AlO_4 tetrahedra parallel to [010] that join together to form small and large channels that are also parallel to [010] (Kocman et al. 1974; Bissert and Liebau 1986). The H_2O molecules occur inside the larger channel and build infinite one-dimensional chains (Fig. 1; Kocman et al. 1974; Ståhl et al. 1989; Quartieri et al. 1999). The H_2O molecules are hydrogen bonded to each other with $H\cdots O_w$ distances of 1.949(3) Å and 1.955(3) Å at 13 K and 1.997(6) Å and 2.002(5) Å at 295 K, whereas the H···O (framework) distances are in the range of 2.544(4) to 2.946(4) Å (Ståhl et al. 1989). This construction has led to the description of the H_2O chains in bikitaite as "one-dimensional ice" (Quartieri et al. 1999). However, there are two notable characteristics of the infinite H_2O chains that differentiate them from H_2O in ice or water: (1) only one hydrogen atom of the H_2O molecule takes part in hydrogen bonding and (2) the H_2O chain is pinned to the Al-Si framework channel wall through bonding between the O_w atom of the H_2O molecule and a Li atom. Thus, the effect of temperature on the hydrogen bond, OH···O, will be largely controlled by extension or contraction of the bikitaite framework along [010].

In bikitaite the H_2O states are intermediate in complexity as compared to the relatively simple "zero-dimensional" case in end-member beryl and cordierite. Here, single non-hydrogen-bonded H_2O molecules occur in small structural cavities and have little interaction with the silicate framework (Kolesov and Geiger 2000a; Kolesov and Geiger 2000b). In most zeolites the case is more complicated, because there are large cavities where H_2O molecules interact with the surroundings in various ways and thus the H_2O molecules are distorted (e.g., Kvick 1986).

There have been a large number of vibrational spectroscopic studies of the H_2O molecule and hydrogen bonding in different substances (see Jeffrey 1997 for a review). The nature of hydrogen bonding in liquids and solids is better understood today after many years of uncertainty and confusion. However some questions still remain. Among them, the nature of the linewidths or line broadening of O-H stretching modes in IR and Raman spectra is not completely understood. Hadzi and Bratos (1976) proposed the following mechanisms for causing line broadening in systems having weak and moderately strong hydrogen bonds: (1) structural disorder that produces a range of hydrogen bonded interactions (e.g., formation of different types of hydrogen bonded aggregates); (2) Fermi resonance; (3) anharmonicity leading to strong coupling between high wavenumber (A-H) and lower wavenumber (AH···B) vibra-

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* E-mail: chg@min.uni-kiel.de

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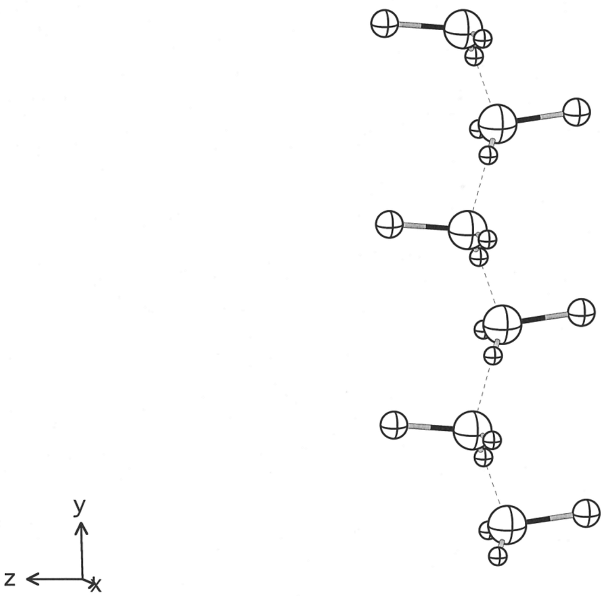


FIGURE 1. Infinite H_2O chain in the structural channels parallel to [010] in bikitaite. The medium sized spheres are Li cations bonded to the O atoms (large spheres) of the H_2O molecules. Only one of the hydrogen atoms is bonded to a neighboring H_2O molecule.

tions. It should be noted that the first two cases do not necessarily reflect the physical properties of the hydrogen bond itself, and they can affect, in principle, any phonon independently of any hydrogen bonding. Anharmonicity is an important factor that can give rise to phonon line broadening in vibrational spectra (Bratos et al. 1991).

There has been very little vibrational spectroscopic (i.e., IR and Raman) work done on bikitaite. Quartieri et al. (1999) presented unpolarized IR spectra showing OH bands at room temperature, but no specific mode assignments were made. The dynamics of the H_2O molecule were investigated by ^{1}H NMR spectroscopy (Larsson et al. 1989) and the static and dynamic properties of the H_2O chain in bikitaite were simulated using ab initio calculations (Fois et al. 2001). The work herein was undertaken to investigate the vibrational and bonding properties of the H_2O molecules. In order to do this in a through way, single-crystal polarized Raman spectra were measured over a wide spectral (40–4000 cm^{-1}) and temperature (5–625 K) range.

EXPERIMENTAL METHODS

The bikitaite crystals investigated are from Bikita, Zimbabwe and are those used in the crystal structure refinement study of Bissert and Liebau (1986). Polarized Raman spectra were recorded with a Triplemate SPEX spectrometer with a CCD detector (model LN-1340 PB) from Princeton Instruments. The 514.5 or 488 nm lines of an Ar laser were used for the spectral excitation. The spectra were measured in 90° or 180° collection geometry. The low-temperature spectra were recorded by fixing the crystal on a cold finger of a helium cryostat from the company “Air Products” and the precision of the measured temperatures is estimated to be ±1 K at temperatures lower than RT and ±5 K above RT. All measurements were performed with a spectral resolution of 5 cm^{-1}.

SYMMETRY ANALYSIS

The space group of bikitaite is $P1$, with $Z = 1$ (Kocman et al. 1974 proposed space group $P2_1$, but the more recent studies, Bissert and Liebau (1986), Ståhl et al. (1989), and Quartieri et al. (1999), give $P1$ in which the Al and Si cations show a high degree of order). The low symmetry means that all possible optic vibrations, a total of 75, are Raman and infrared active with any polarization direction of the exciting light. The molecular H_2O vibrations should be characterized by two high wavenumber O-H stretching modes that are not hydrogen bonded (i.e., in-phase and out-of-phase), two O-H stretching modes that are associated with hydrogen bonding at lower wavenumbers, and by bending modes and external vibrations of H_2O.

EXPERIMENTAL RESULTS

Figure 2 shows the unpolarized Raman spectrum between about 50 and 1200 cm^{-1} at 5 K illustrating the lattice vibrations arising from the framework of bikitaite. Figures 3a and 3b show polarized single-crystal spectra with different polarization settings in the wavenumber region 3200 to 3800 cm^{-1} at 5 and 295 K, respectively, where the O-H stretching vibrations occur. There are four observable bands in the low-temperature spectra at 3372, 3448, 3579, and 3597 cm^{-1}. The modes are broadened at 295 K and the two high wavenumber modes are indistinguishable at this temperature. A fifth weak, broad band at 3268 cm^{-1}, about twice the energy of an H_2O bending mode(s) (Fig. 4), whose intensity is probably enhanced through Fermi resonance, is observed in the (*bb*) spectrum at 5 K. Raman spectra between 5 K and 300 K showing the temperature dependence of the O-H vibrations are shown in Figure 5. Figures 6 and 7 show the temperature dependence of the wavenumbers

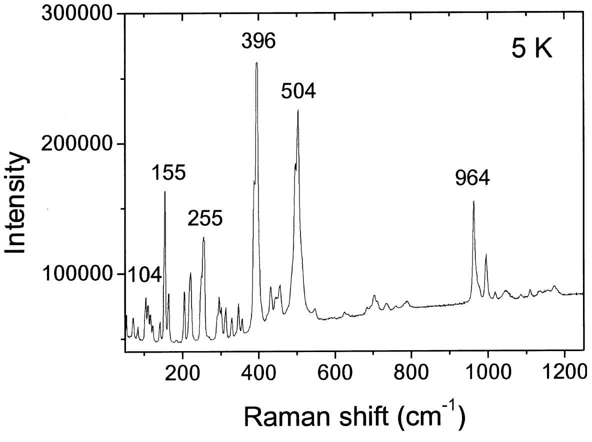


FIGURE 2. Unpolarized 5 K Raman spectrum showing the framework vibrations.

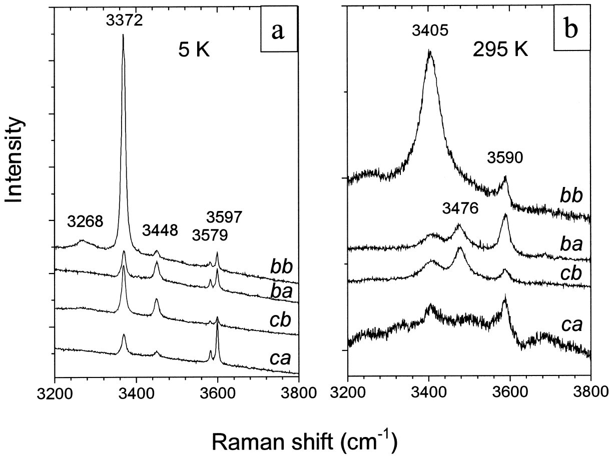


FIGURE 3. Polarized single-crystal Raman spectra taken at 5 K (**a**) and 295 K (**b**).

and half widths of the two strongest O-H stretching modes and also two representative lattice modes obtained after fitting with Lorentzian peaks. The wavenumber of the hydrogen-bonded O-H stretching mode increases from 3372 cm^{-1} at 5 K to 3415 cm^{-1} at 300 K. In contrast, the energy of the O-H stretching mode at 3597 cm^{-1} shifts only slightly with temperature. Their linewidth behavior as a function of temperature is also different (Fig. 7a). Figure 7b shows the linewidths of two lattice modes. It is important to note that line broadening of all modes, as well as changes in their energies, starts at approximately the same temperature around 50 K (Figs. 6 and 7). Unpolarized spectra in the high wavenumber region between room temperature and 620 K are shown in Figure 8.

DISCUSSION

Mode assignments and line widths

An interpretation and assignment of the vibrational modes related to the H_2O molecules in bikitaite can be made using structural information (i.e., bond lengths and angles) obtained from neutron diffraction measurements (Ståhl et al. 1989). The diffraction data show that the two crystallographically independent H_2O molecules have intramolecular H-O-H angles of 104.6(3)° and 104.2(4)° and O-H distances of 0.960(3) Å and 0.961(3) Å at 13 K. A free H_2O molecule in the gas phase has an angle of 104.52° and an O-H distance of 0.9572 Å (Eisenberg and Kauzmann 1969). The hydrogen bonds of the H_2O chains are nearly linear with O-H···O angles of 171.5(3)° and 169.9(3)° for the two molecules. Thus, the H_2O molecules in bikitaite are undisturbed in comparison to those located in the cavities of other zeolites (Ståhl et al. 1989). Bikitaite appears to represent a rare situation where an *ordered* one-dimensional hydrogen-bonded chain of H_2O molecules occurs. To the best of our knowledge such an arrangement has not been described in minerals before. One-dimensional H_2O chains have been found in the synthetic zeolite Li-A(BW) (Krogh Anderson and Ploug-Sørensen 1986) and is recognized in three other nonsilicate phases ($LiHC_8H_8O_4{\cdot}2H_2O$, $LiHCOO{\cdot}H_2O$, and $HCl{\cdot}3H_2O$), all of which are synthetics (Kim and Küppers 1994). The H_2O molecules in bikitaite are not completely free as the O_w atoms are bonded to Li cations that extend partly into the channels. The Li cations are also bonded to three framework O atoms producing a tetrahedral coordination.

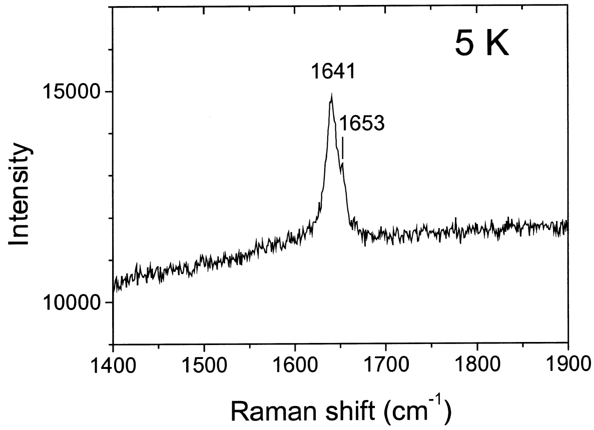


FIGURE 4. Unpolarized single-crystal Raman spectrum in the wavenumber range of the H_2O bending vibrations at 5K.

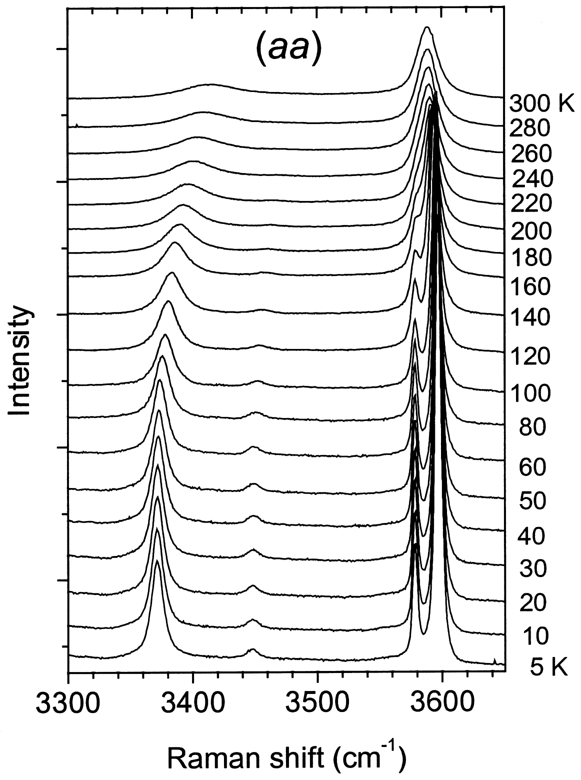


FIGURE 5. Raman (*aa*) spectra of O-H stretching vibrations in the temperature range 5–300 K.

One unit cell of bikitaite containing weakly bound H_2O molecules has $m = 2$ molecular units and $N = 6$ atoms. The total number of vibrations is $3N - 3 = 15$ (3 acoustic modes are not counted) with $3m = 6$ rotational modes and $(3m - 3) = 3$ translational modes. Six internal vibrations remain, 2 bending

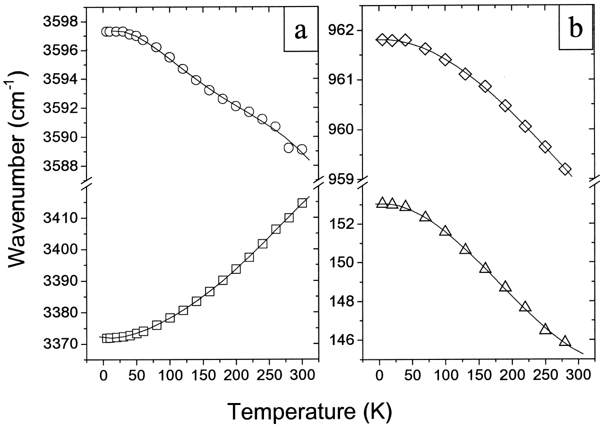


FIGURE 6. Wavenumber of O-H stretching modes at about 3370 and 3600 cm^{-1} (**a**) and lattice modes at 150 and 960 cm^{-1} (**b**) vs. temperature.

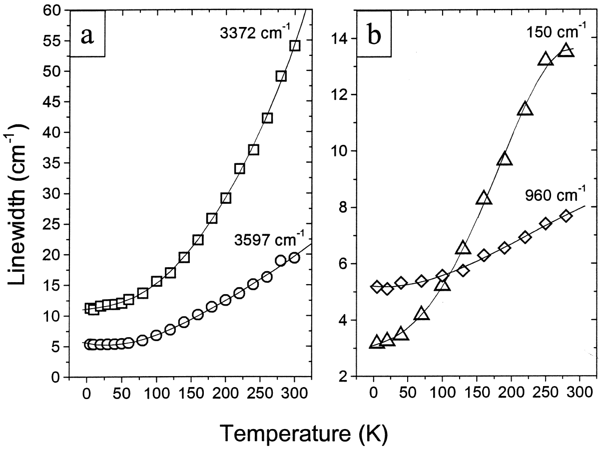


FIGURE 7. Linewidths of O-H stretching modes at about 3370 and 3600 cm^{-1} (**a**) and lattice modes at 150 and 960 cm^{-1} (**b**) vs. temperature.

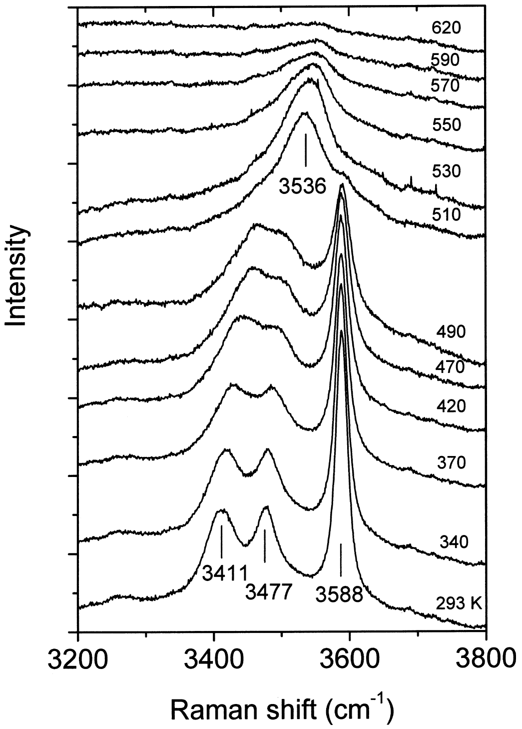
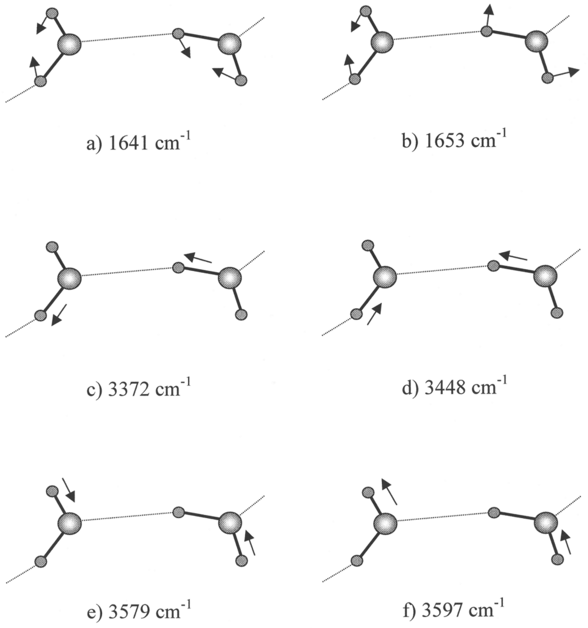


FIGURE 8. Unpolarized spectra in the high wavenumber region between room temperature and 620 K.



a) 1641 cm^{-1}
b) 1653 cm^{-1}
c) 3372 cm^{-1}
d) 3448 cm^{-1}
e) 3579 cm^{-1}
f) 3597 cm^{-1}

FIGURE 9. H_2O molecular vibrations in bikitaite. The left column shows the in-phase vibrations and the right column the out-of-phase vibrations. (**a** and **b**) Bending vibrations. (**c**–**f**) Stretching vibrations.

modes and 4 stretching modes (in-phase and out-of-phase). All of the external and internal modes have *A*-type symmetry. The mode assignments are shown in Figure 9. At 5 K there are two high wavenumber in-phase and out-of-phase O-H stretching vibrations at 3579 and 3597 cm^{-1}, respectively, that have no hydrogen bonding, and two lower wavenumber O-H stretching modes at 3372 and 3448 cm^{-1} that are hydrogen bonded. This follows from the well-known relationship that the O-H stretching energy is a function of the OH···O (or O···O) distance (e.g., Novak 1974; Jeffrey 1997). That is, the higher the energy of an O-H stretching mode, the weaker the hydrogen bonding, OH···O. These assignments are also consistent with the temperature behavior of these two pairs of modes. The lower wavenumber O-H stretching modes increase in energy with increasing temperature and thus hydrogen bonding weakens. The two higher wavenumber O-H stretching modes, in contrast, change little with temperature. This indicates that the associated OH groups have no or very little interaction with other molecules or the crystal framework. At room temperature three O-H stretching bands are observed at 3405, 3476, and 3590 cm^{-1}, which can be compared to the values of 3401, 3471, and

3579 cm^{-1} as determined by IR spectroscopy (Quartieri et al. 1999).

The linewidth of the 3372 cm^{-1} mode is narrow, about 11 cm^{-1} around 5 K (Fig. 7a). Hydrogen bonding does not give rise to line broadening. This is not an unexpected result and is observed in other systems containing H_2O molecules (see Hadzi and Bratos 1976 for a review). What is somewhat surprising is that the linewidth of this mode is still relatively narrow, about 54 cm^{-1} at room temperature (Fig. 7a). There are many examples in the literature where the linewidths of H_2O modes having hydrogen bonding are as broad as a few hundred cm^{-1} at room temperature (Hadzi and Bratos 1976; Bratos et al. 1991).

Another important observation that follows from the temperature behavior of all modes (i.e., lattice, as well as hydrogen bonded and non-hydrogen bonded O-H vibrations) is that the mode energies and linewidths begin to change at about the same temperature around 50 K. Here the Boltzmann population of low-wavenumber lattice modes begins to increase. Consequently, we propose that the broadening of hydrogen-bonded O-H stretching modes with increasing temperature is linked to the thermal behavior of the atoms of the H_2O molecules in the chains. One can propose the following "adiabatic model" to account for the linewidth behavior of the hydrogen-bonded OH modes. At low temperatures, say around 50 K, only low-energy vibrational states are populated (i.e., 20–40 cm^{-1}) and they modulate the O···O distance (i.e., potential) in the H_2O chain. The energy of an O-H stretching mode is, by comparison, much greater and thus the hydrogen atom in an OH group can undergo several vibrations while the O···O distance remains unchanged. The "instantaneous" energy of an O-H vibration is thus governed by an O···O potential that describes an "instantaneous" O···O distance. The low-energy thermal vibrations of the O atoms thereby cause a change in the potential associated with the hydrogen bonding resulting in a range of O-H stretching mode energies. If the magnitudes of the vibrational displacements of the O···O atoms at some temperature are known, one can calculate the corresponding OH linewidth using the OH wavenumber-O···O distance relationship (Novak 1974). This value can be compared to the experimentally measured linewidths (Fig. 7a) and the adiabatic model tested. Ståhl et al. (1989) measured the atomic displacement parameters of the atoms of the H_2O molecules at 13 K and 295 K through neutron diffraction. Because the H_2O chain in bikitaite is parallel to [010], it is enough to consider the β_{22} displacement parameters of neighboring O17 and O27 atoms comprising an OH···O bond. The sum of $\beta_{22}(O17) + \beta_{22}(O27)$ is 0.0098 Å at 13 K and 0.0442 Å at 295 K (Ståhl et al. 1989). The change in OH wavenumber with respect to the change in O···O distance, $\Delta\nu_{OH}/\Delta R_{O\cdots O}$, is about 1180 cm^{-1}Å^{-1} for an O-H stretching mode in the wavenumber region around 3400 cm^{-1} and for an O···O distance of ~2.8–2.9 Å (Novak 1974). From this and the displacement parameter data, the linewidth of the lowest wavenumber hydrogen-bonded OH band is calculated to be 11.6 cm^{-1} at 13 K and 52.2 cm^{-1} at 295 K. The experimentally measured OH line widths in the Raman spectra are 11.2 and 52.5 cm^{-1}, respectively (Fig. 7a). The good agreement between experimental and calculated values supports the adiabatic model, and thus our proposed model for OH-mode broadening appears valid.

The model is applicable to bikitaite, because the H_2O molecules in the chains are *ordered* and have single hydrogen bonds. In ice I_h, in comparison, the O-H stretching band envelope at about 3220 cm^{-1} has a line width of about 500 cm^{-1} (Eisenberg and Kauzmann 1969). Here the H_2O molecules have a disordered arrangement of hydrogen atoms that produce a range of O···O distances. Mode coupling also plays a role in causing line broadening in ice. The situation in liquid water is similar, where the Raman spectrum shows a broad asymmetric band with a maximum at 3439 cm^{-1} and a line width of 407 cm^{-1} (Eisenberg and Kauzmann 1969). In both ice and water, structural disorder produces a continuum of energetic states that gives rise to major line broadening of the O-H stretching vibrations.

It should be noted that no combination modes consisting of high wavenumber O-H stretching and low wavenumber OH···O vibrations, which typically characterize anharmonic hydrogen-bonded systems, are observed at any temperature in the spectrum of bikitaite. Thus, strong anharmonicity cannot account for the observed OH line broadening. The OH···O bonds in bikitaite are characterized by weak or at most intermediate strength hydrogen bonding; O···O thermal motion is responsible for causing the broadening of the O-H stretching modes. The adiabatic model is less valid when the ratio of the A-H and AH···B energies decreases, as may occur in other systems with stronger hydrogen bonding.

Behavior of H_2O above room temperature

The Raman spectra show a change in bonding in the H_2O chain at about 500 K. With increasing temperature, the two lower wavenumber OH bands increase in energy and that of the intense band at 3588 cm^{-1} decreases. Around 500 K a single band at 3536 cm^{-1} is observed. The spectrum is typical for that of a H_2O molecule bonded to a cation via an O atom (see Kolesov and Geiger 2000b for the case of Class II H_2O in cordierite). Only the symmetric H_2O vibration (ν_1) is observed and its energy is shifted to lower wavenumbers compared to its value in a free H_2O molecule (e.g., Falk et al. 1986). Above 500 K dehydration begins. Kocman et al. (1974) made DTA and TGA measurements on bikitaite and observed a weight loss starting around 375 K with a maximum in the DTA curve around 550 K and ending around 770 K. The Raman spectra from our heating experiments show that by 620 K bikitaite is almost H_2O free.

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