

## Identification of a low-energy OH-valence vibration in zoisite

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### Abstract

By using the H–D isotope effect on the vibrational spectrum of orthorhombic zoisite, we confirm the assignment of a band at  $2160\text{ cm}^{-1}$  to a low-energy OH-stretching vibration. These OH groups occur in strong hydrogen bridges with a bonding energy of approximately  $40\text{ kJ/mole}$ , along with the “normal” OH groups in the O(10)–H  $\cdots$  O(4) bridge. Furthermore, four OH librational modes could be identified in the region below  $1100\text{ cm}^{-1}$ . The samples studied by IR spectroscopy were synthesized at 14 kbar and  $700^\circ\text{C}$  in the systems CaO– $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$ – $\text{H}_2\text{O}$  and  $-\text{D}_2\text{O}$ , respectively.

### Introduction

According to most papers dealing with the crystal chemistry of orthorhombic zoisites,  $\text{Ca}_2\text{Al}_3[\text{O}(\text{OH})(\text{SiO}_4)(\text{Si}_2\text{O}_7)]$ , all protons are bonded to O(10) of the structure (Dollase, 1968) and form a hydrogen bridge O(10)–H  $\cdots$  O(4). This was concluded on the basis of (1) crystal chemical arguments, (2) bond-strength calculations for oxygen atoms (Dollase, 1968), and (3) infrared experiments using oriented crystal sections and polarized radiation (Linke, 1970). The O(10)–H dipoles give rise to an  $\nu_{\text{OH}}$  valence vibration at about  $3160\text{ cm}^{-1}$  (Linke, 1970).

In addition to this absorption band, Langer and Raith (1974) found a band at  $2160\text{ cm}^{-1}$  in the high-energy part of spectra of all zoisites they studied. The authors tentatively assigned this band to a second type of OH groups forming very strong hydrogen bridges O(x)–H  $\cdots$  O(y). However, because it was uncertain which oxygen atoms of the zoisite structure are involved, this band assignment remained doubtful. We now report infrared results obtained with OH- or OD-bearing synthetic zoisites, which assign the inferred  $\nu_{\text{OH}}$  at  $2160\text{ cm}^{-1}$ .

The correct assignment of this band can be proved from the isotope effect on valence vibrations: in a

first approximation, such vibrations can be treated on the basis of the harmonic oscillator theory, which gives

$$\tilde{\nu} = \frac{\sqrt{f}}{2\pi c} \sqrt{\frac{1}{m_1} + \frac{1}{m_2}}$$

for the wavenumber  $\tilde{\nu}$  of the stretching vibration of a two-atomic group with  $m_1$  and  $m_2$ , the atomic masses,  $f$ , the force constant, and  $c$ , the vacuum light velocity. Assuming the same force constant for the O–H and O–D stretching vibrations, one obtains:

$$\tilde{\nu}_{\text{OH}}/\tilde{\nu}_{\text{OD}} = 1.3744$$

This means all vibrations due to OH groups should shift approximately by a factor of  $1/1.3744$  towards lower wave numbers, when hydrogen is substituted by deuterium. As a first rough approximation, this holds also for librational modes of the OH groups occurring at around  $1000\text{ cm}^{-1}$  and below. Therefore, such vibrations may possibly also be identified in zoisite, along with the valence vibrations.

### Experimental methods and characterization of synthetic samples

Zoisites were synthesized in the presence of an excess of either water or deuterium oxide from a start-

ing mixture which consisted of a CaO–SiO<sub>2</sub> glass plus alumina and was prepared and stored with care to avoid traces of H<sub>2</sub>O. Starting materials were:

- (1) Glass with the composition 2CaO · 3.23SiO<sub>2</sub> (Anastasiou and Langer, 1977). Glass was preferred as a calcium source over CaCO<sub>3</sub> to escape eventual difficulties with additional absorption bands generated by CO<sub>3</sub><sup>2-</sup> or CO<sub>2</sub> traces in the run products.
- (2) Alumina prepared as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from 99.95% Al metal (Merck, Darmstadt) and fired for four hours at 1000°C immediately before preparing the mixture. After firing, the material consisted mainly of corundum with slightly broadened X-ray reflections and a little  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.
- (3) Deuterium oxide, 99.75% D<sub>2</sub>O (UVASOL, Merck, Darmstadt).

Synthesis runs of approximately one-day duration were performed in gold capsules in a piston cylinder apparatus at 700°C and 14 kbar. In runs aimed at synthesizing the deuterated form, the charge capsule was enclosed in a larger gold capsule also containing starting material plus D<sub>2</sub>O. This double-capsule technique was applied to prevent possible hydrogen diffusion from the high-pressure cell into the charge capsule.

All run products consisted of orthorhombic zoisite and minor amounts of quartz on the basis of X-ray and optical examination. Zoisite formed tiny prismatic crystals with lengths of up to 20  $\mu$ m. Because of the small crystal size, it was impossible to decide which form,  $\alpha$ - or  $\beta$ -zoisite, was present. However, as the zoisites were synthesized in the iron-free system, it is reasonable, on the basis of literature information (*cf.* Winchell, 1933, p. 311; Tröger, 1967, p. 318–319), to assume that they are of the  $\alpha$ -form. The X-ray powder diagrams of the deuterated and hydrogenated zoisites are identical and hence the lattice constants are the same within the limits of error (Table 1).

Infrared spectra were recorded at room temperature by means of a Perkin-Elmer 325 spectrophotometer on powder samples embedded in KBr pellets.

A blank KBr pellet was used in the reference beam.

#### Infrared spectra and their interpretation

Spectra in the high-energy region above 1500 cm<sup>-1</sup> of orthorhombic zoisites synthesized with excess water or deuterium oxide are shown in Figure 1. The low-energy region below 1200 cm<sup>-1</sup> is shown in Figure 2.

The spectra A of the OH-bearing form show all the band maxima and shoulders at the same energies as the ortho-zoisite spectra presented by Langer and Raith (1974), including the "critical" band No. 4 at 2160 cm<sup>-1</sup>. No additional bands originating from the small quartz contaminant (see above) can be detected in the present spectra of Figure 2. The same is partially true for spectra B of the deuterated form. However, characteristic differences occur between the latter and the normal OH-zoisites.

In the high-energy region above 1500 cm<sup>-1</sup>, the spectra of zoisites synthesized with D<sub>2</sub>O differ from those of the OH-form in the following features:

- (1) Band No. 2 of the OH-form (3150 cm<sup>-1</sup>) and its satellites Nos. 1 and 3 exhibit much lower intensities. Concomitantly, the intensity of the "critical" band No. 4 of the OH-form (2160 cm<sup>-1</sup>) decreases also, so that it almost disappears.
- (2) A new intense band with two satellites appears at 2362 cm<sup>-1</sup>, which is related to band No. 2 in the OH-form by the factor 3150/2362 = 1.33, *i.e.* a value close to the theoretical factor  $\tilde{\nu}_{\text{OH}}/\tilde{\nu}_{\text{OD}} = 1.3744$ . Furthermore, a small new band is observed at 1608 cm<sup>-1</sup>, which is related to the "critical" band No. 4 in the OH-form by a factor of 2165/1608 = 1.35, which again is near the theoretical value.

At first glance, the small 1608 cm<sup>-1</sup> band of the deuterated form could be thought as originating from the bending modes  $\delta$  of adsorbed water. However, this can be excluded for three reasons: (1) the maximum of the water bending  $\delta$  occurs at slightly higher energies of about 1640 cm<sup>-1</sup> (*cf.* spectrum A); (2) the half-width of the 1608 cm<sup>-1</sup>

Table 1. Lattice constants of synthetic zoisites. Data obtained from powder diffractograms with Si as internal standard

Sample No.	Synthesized with	a <sub>o</sub> (Å)	b <sub>o</sub> (Å)	c <sub>o</sub> (Å)	V <sub>o</sub> (Å <sup>3</sup> )	No. of reflections	No. of hkl
PZO 2	H <sub>2</sub> O	16.193 ± 0.002	5.549 ± 0.001	10.036 ± 0.002	901.8 ± 0.1	36	43
PZO 1	D <sub>2</sub> O	16.194 ± 0.002	5.550 ± 0.001	10.036 ± 0.002	902.0 ± 0.1	36	43

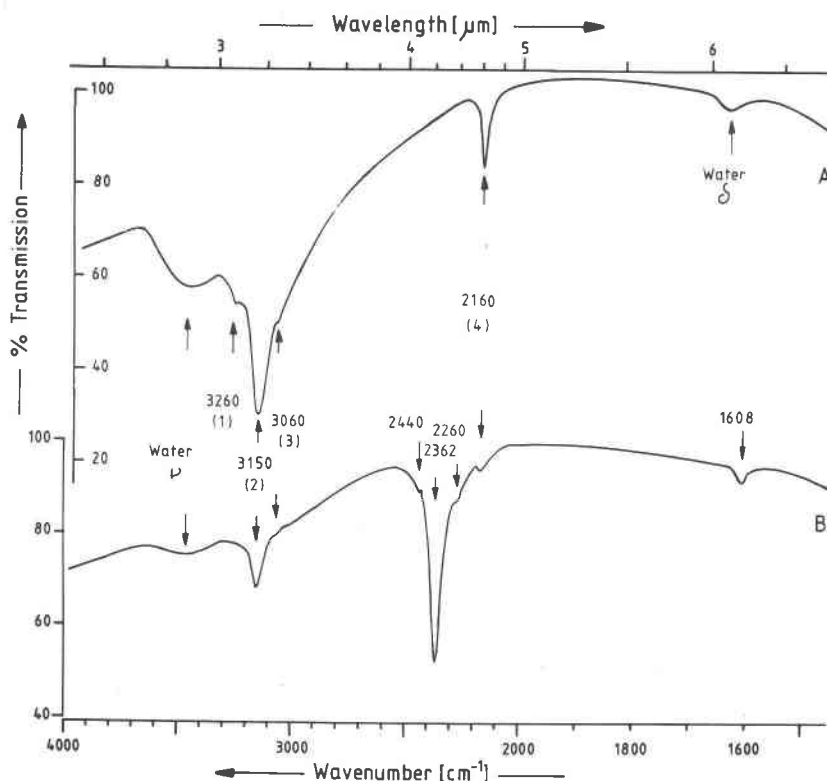


Fig. 1. Infrared absorption spectra in the high-energy region above  $1500\text{ cm}^{-1}$  of orthorhombic zoisites synthesized with  $\text{H}_2\text{O}$  (A) and  $\text{D}_2\text{O}$  (B). Wavenumbers are given for the OH vibrations, spectrum A, and the new bands occurring in spectrum B of the sample synthesized with  $\text{D}_2\text{O}$ . Numbers in brackets are the same as in Langer and Raith (1974). The diffuse bands designated by "water  $\nu$ " and "water  $\delta$ " are caused by valence and bending vibrations, respectively, of traces of adsorbed water.

band is much smaller than that of the water bending; (3) spectrum B of the deuterated form exhibits only a very weak band in the region of the valence vibrations  $\nu$  of adsorbed water. As the intensity ratio of  $\nu$ - and  $\delta$ -bands of adsorbed water is high (*cf.* spectrum A),  $\delta$  certainly cannot be observed in spectrum B.

These observations show that the "critical" band No. 4 at  $2160\text{ cm}^{-1}$  is indeed due to a low-energy OH-valence vibration. This implies that not all protons of the zoisite formula are bonded to the O(10), forming the O(10)-H  $\cdots$  O(4) bridge. Some of the protons are indeed allocated in another, much stronger O(x)-H  $\cdots$  O(y) bridge. The above observations also show that the zoisite synthesized with  $\text{D}_2\text{O}$  is not fully deuterated and still contains some OH groups in both bridges, although precautions were taken to avoid water in the runs performed in the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-D}_2\text{O}$  system, except with the  $\text{D}_2\text{O}$  itself which contained 0.25%  $\text{H}_2\text{O}$ . The system thus contained only trace amounts of water. On the other hand, the intensity ratio  $T_{\nu_{\text{OD}}}/T_{\nu_{\text{OH}}}$  is approximately

3.5. Therefore, the value of the distribution coefficient

$$K_D = \frac{[\text{OD}]_{\text{cryst}} \cdot [\text{OH}]_{\text{fluid}}}{[\text{OH}]_{\text{cryst}} \cdot [\text{OD}]_{\text{fluid}}}$$

must be low.

In the low-energy region, below  $1200\text{ cm}^{-1}$  (Fig. 2), most of the band maxima and shoulders are displayed with the same energies and relative intensities in the spectra of both the OH- and the (OD,OH)-form. They do differ in the following features:

- (1) The deuterated form exhibits additional bands with relatively high intensity at 815 and  $730\text{ cm}^{-1}$ . Both new bands obscure bands No. 16 and No. 17, which, therefore, appear only as shoulders in the (OD,OH)-form. The new  $730\text{ cm}^{-1}$  band is relatively broad, because it almost coincides with band No. 18 at  $717\text{ cm}^{-1}$ . A third additional band, with lower intensity, occurs at  $705\text{ cm}^{-1}$  in the (OD,OH)-form.
- (2) Band No. 19 at  $695\text{ cm}^{-1}$  of the OH-form is much weaker in the deuterated form and seems to ap-

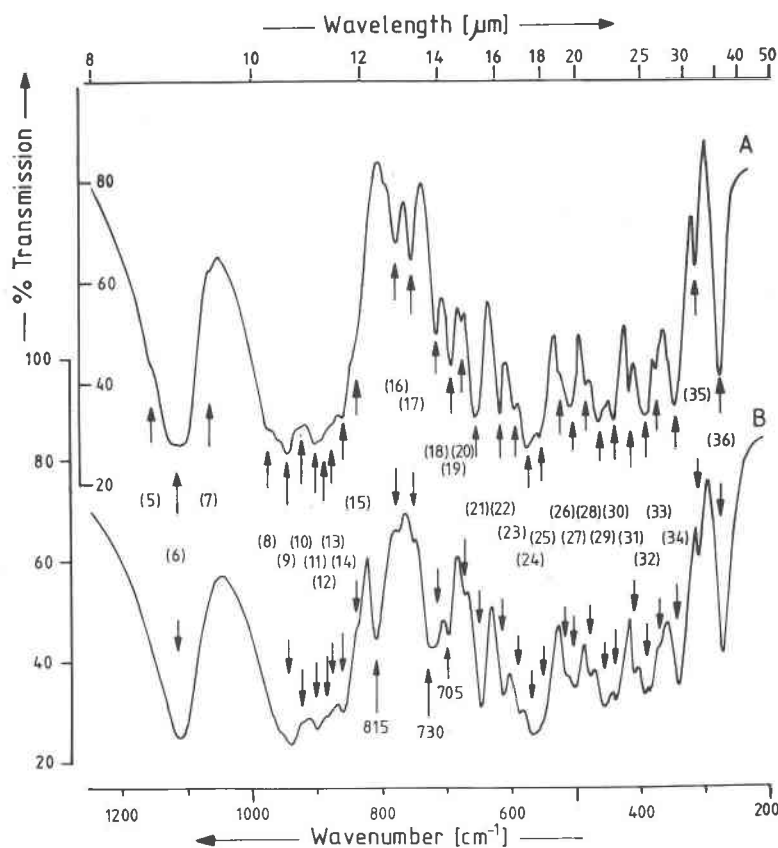


Fig. 2. Lattice vibrational region of the zoisite spectra. A, B, and numbers as in Fig. 1.

pear only as a small shoulder at the low-energy wing of the band at  $705\text{ cm}^{-1}$ .

The new bands of the (OD,OH)-form, mentioned under point 1, can only be interpreted as OD-librational modes. Therefore, one should expect a concomitant decrease in the intensities of the corresponding OH-librational modes. However, no such intensity changes are clearly discernible when comparing spectra A and B of Figure 2. Applying the  $\bar{\nu}_{\text{OH}}/\bar{\nu}_{\text{OD}}$ -factor 1.34 as a first approximation in the present case of the librational modes, the expected OH-bands may be calculated from the above OD-band maxima to occur at about 1090, 975, and  $945\text{ cm}^{-1}$ , respectively. Perhaps the presence of a band at  $1090\text{ cm}^{-1}$  could account for the shoulder 5 and the greater width of band No. 6 in spectrum A of the OH-form. In spectrum A, the shoulder at about  $975\text{ cm}^{-1}$  (band No. 8) is stronger than in spectrum B and might therefore be interpreted as the expected second OH-libration. No observation in spectrum A can account for the third OH-libration expected at about  $945\text{ cm}^{-1}$ . The lack of band No. 19 in spectrum B (*cf.* point 2) could indicate that this band is due to a fourth OH-librational mode. If so, the corresponding

OD-band is to be expected at around  $520\text{ cm}^{-1}$ , *i.e.* coinciding with shoulder No. 26.

The two types of OH groups causing stretching modes at  $3160$  and  $2130\text{ cm}^{-1}$  are bonded in hydrogen bridges  $\text{O}(10)\text{-H}\cdots\text{O}(4)$ , I, and  $\text{O}(x)\text{-H}\cdots\text{O}(y)$ , II, respectively. When the two oxygen atoms in such bridges lie on a mirror plane, which is at least true for the first bridge I,<sup>1</sup> two principal librational modes can be expected, namely an in-plane mode at lower energies and an out-of-plane mode at higher energies (*cf.* Vedder and McDonald, 1963). Therefore, with the two bridges present, a maximum of four librational bands may occur in zoisite. As hydrogen bonding is much stronger in bridge II than in bridge I (Langer and Raith, 1974), the two librational modes of the former bridge should have higher energies than those of the latter one. Therefore, we tentatively assign the four bands discussed above as follows:  $815\text{ cm}^{-1}$  (D-form),  $1090\text{ cm}^{-1}$  (H-form): out-of-plane, bridge II;  $730\text{ cm}^{-1}$  (D-form),  $975$  (H-form): out-of-plane, bridge I;  $705\text{ cm}^{-1}$  (D-form),  $945$  (H-form): in-

<sup>1</sup> O(10) and O(4) are in position 4c with point symmetry  $m$  of space group  $Pnma$  (Dollase, 1968)

plane bridge II; and 520 (D-form), 695 (H-form): in-plane bridge I.

### Summary and conclusion

This infrared study of hydrogenated and deuterated zoisites confirms that the band at  $2160\text{ cm}^{-1}$ , found by Langer and Raith (1974) in zoisites and lacking in clinozoisites, certainly originates from a low-energy O–H stretching mode. These OH groups occur in a second, very strong hydrogen bridge, O(x)–H  $\cdots$  O(y), in addition to the normal O(10)–H  $\cdots$  O(4) bridge, already recognized in the literature, which means that the last contains statistically less than one proton per formula unit, provided not more than one is found by chemical analysis.

Four bands at maximum in the spectral region below  $1200\text{ cm}^{-1}$  could be identified as OH-librational modes and tentatively be assigned to in-plane and out-of-plane modes in the two hydrogen bridges.

From the energy of the O(x)–H stretching band at  $2160\text{ cm}^{-1}$ , an O(x)–O(y) distance of  $2.56\text{ \AA}$  was calculated (Langer and Raith, 1974). On the basis of the theoretical treatment of hydrogen bridges in a one-dimensional model (Lippincott and Schroeder, 1955), this distance would result in an energy of ap-

proximately  $40\text{ kJ/mole}$ . This unusually high hydrogen bond energy could contribute to a stabilization of orthozoisite vs. clinozoisite in the iron-free system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ .

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