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Refined relationship between the position of the fundamental OH stretching and the first overtones for clays

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Abstract The aim of this paper is to determine a relationship between the wavenumbers of the first OH-stretching overtones ($W_{2\nu\text{OH}}$) and the wavenumbers of the OH-stretching fundamentals ($W_{\nu\text{OH}}$) to help to interpret the near-infrared (NIR) spectra. The first overtone ($2\nu\text{OH}$) bands appear at wavenumbers less than twice those of the fundamental bands (νOH), due to the anharmonic character of vibrations, $X = W_{2\nu\text{OH}}/2 - W_{\nu\text{OH}}$, with X being the anharmonicity constant. Talc samples with various crystal chemistries are used to solve the equation and the experimental data are well fitted with $X = -85.6 \text{ cm}^{-1}$. As far as the authors are aware, it is the first time that the anharmonicity constant for the OH-stretching vibrations is determined for phyllosilicates. The anharmonicity constant remains almost unchanged for several types of clay samples. Therefore the relation, established from talc samples because their absorption bands are narrow and their wavenumber range of OH vibrations is wide, can be used for any other clay minerals.

Keywords Infrared spectroscopy · Near-infrared spectroscopy · Clay minerals · Anharmonicity · Crystal chemistry

Introduction

Clay minerals show various chemical compositions according to numerous cationic substitutions occurring in their tetrahedral and octahedral sheets and their interlamellar space, (e.g. Weaver and Pollard 1973). Chemical analyses are based on an average of at least several hundred millions of unit cells and the deduced structural formulae do not therefore necessarily reflect the actual crystal chemistry of clays. Indeed, the analytically determined cations must be correctly distributed over the available structural sites. Particular difficulty arises from the occurrence of either impurities (e.g. Madejová and Komadel 2004) or occurrence of trivalent cations which can occupy both octahedral and tetrahedral sites (e.g. Petit et al. 2004). Among the many analytical techniques available, the utility of Fourier transform infrared (FTIR) spectroscopy in this respect is unique because even if impurities are present, the spectral fingerprint for the element of interest is related to the average local structure. In addition to identification of minerals present, it is possible to relate spectral information directly to the specific chemistry of the mineral. Moreover, unlike other spectroscopies, FTIR spectroscopy allows to samples of any chemical composition to be analyzed. For example, nuclear magnetic resonance can be used to investigate only samples with low Fe contents, whereas ^{57}Fe -Mössbauer, or Fe $K\alpha$ X-ray absorption spectroscopies provides information only on local environments around Fe (e.g. Gates et al. 2002).

The vibrations of layer silicates can be approximately separated into those of constituent units, i.e. the OH groups, the silicate anion, the octahedral cations and the interlayer cations if any. Among these, the vibrations of the OH groups are the most fully understood and employed because they are very sensitive indicators of the OH environment. Based on quantitative results obtained previously for various clay minerals, the absorption coefficients of OH vibration bands are assumed to be constant whatever the local chemistry around OH

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groups (e.g. Slonimskaya et al. 1986; Besson and Drits 1997a, b; Petit et al. 2004). The integrated intensity of each absorption band due to OH groups is then proportional to the number of absorbing centres of each type. Once all the OH vibration bands occurring in the FTIR spectra are correctly attributed, the FTIR spectra can be quantitatively used with clay minerals either to redress structural formula and/or to access cationic distribution in the octahedral sheet (Besson and Drits 1997a; Slonimskaya et al. 1986; Madejová et al. 1994; Cuadros and Altaner 1998; Vantelon et al. 2001; Petit et al. 2004) and tetrahedral sheet (Martin et al. 1992, 1996; Gates et al. 2002). The vibrations of the OH groups most commonly selected are the fundamentals [stretching (ν OH) and bending (δ OH) modes] occurring in the mid-infrared (MIR) region ($4000\text{--}300\text{ cm}^{-1}$). However, the near-infrared (NIR) region ($12\,500\text{--}4000\text{ cm}^{-1}$) where overtones (2ν OH) and combination vibrations (ν OH + δ OH) of the OH group occur are also good markers.

Historically, the NIR (and visible) and MIR fields of research are somewhat distinct from one another. The MIR user is more concerned with functional groups and spectral interpretation than the NIR user, who is often more interested in geostatistical applications. The use of spectral units of cm^{-1} (wavenumber) in the MIR and μm or nm (wavelength) in the NIR is symptomatic of the historical divide separating these communities. Some mineralogical data for clays and clay minerals in the NIR are available (Hunt and Salisbury 1970; Lindberg and Snyder 1972; Hunt et al. 1973), mainly because field and imaging spectrometers and hyperspectral remote sensing work exclusively in the NIR (and visible) region. Indeed, the application of MIR spectroscopy in remote-sensing activities has been restricted, since much of the spectral information occurs only as a small perturbation to the emitted radiation from the Earth's surface, and what is especially relevant to clays is often obscured by absorption of atmospherics (Hunt and Hall 1981). The popularity of NIR spectroscopy has increased greatly in recent years, notably due to the development of detectors able to operate under elevated thermal conditions, and the interpretation work in NIR continues to develop.

Recent results of the NIR region for analyzing the crystal chemistry have significantly extended the

application of IR spectroscopy to clay minerals studies. Indeed, the higher sensitivity to the OH functional group environment of the NIR compared to that of the MIR enables the more effective detection of (1) isomorphous substitutions in talcs (less than 0.01 atom of Fe^{2+} or Al per half unit cell can be detected in the NIR region, while the sensitivity is almost twice as little in the MIR region) (Petit et al. 2004) and nontronites (Gates et al. 2002); (2) fixed Li in reduced-charge montmorillonites (the relative intensity of the trioctahedral OH component is significantly higher in the NIR region than in the MIR region) (Madejová et al. 2000a); (3) Si–OH groups in acid-treated smectites (Pálková et al. 2003). Another use of NIR region is to recalculate the positions of the OH vibrations bands in MIR, as shown by Petit et al. (1999) for the δAlGaOH and δAlCrOH bands in MIR spectra of Ga- and Cr-bearing kaolinities.

The energy required for the first overtone is twice the fundamental, assuming evenly spaced energy levels. Since the energy is proportional to the wavenumber, the first overtone should appear at twice the wavenumber of the fundamental. However, due to the anharmonic character of vibrations (the energy levels are not equidistant), the first overtone bands appear at wavenumbers less than twice these of the fundamental bands (e.g. Herzberg 1945; Kauzmann 1957; Alpert et al. 1964; Barton 2000). The observed bands in the NIR first overtone region are commonly assigned by analogy with the MIR ν OH region (Petit et al. 1999, 2004; Madejová et al. 2000a; Bishop et al. 2002a; Frost et al. 2002a, b; Ferrage et al. 2003). However, to interpret spectra, researchers often need a relationship which allows them to calculate the wavenumbers of the first overtone (2ν OH) in the NIR from the wavenumbers of the fundamental (ν OH) in the MIR and vice versa (Bishop et al. 2002b; Petit et al. 1999; Madejová et al. 2000a; Frost et al. 2001).

This paper aims to furnish a relation for structural OH groups in clay minerals that converts, in wavenumbers, from 2ν OH ($W_{2\nu\text{OH}}$) in the NIR to ν OH ($W_{\nu\text{OH}}$) in the MIR with good precision. To derive the basic correlation between the ν OH and 2ν OH wavenumbers, the selected samples are talcs because their absorption bands are narrow, with few, if any overlapping peaks, and they are sensitive to a variety of

Table 1 Descriptions of the samples used

Samples	Origin	<i>R</i>	No. of samples	<i>x</i>	References
Talc	Natural	Fe^{2+}	15	$0 \leq x \leq 1.02$	Petit et al. (2004)
	$\text{Si}_4(\text{Mg}_{3-x}\text{R}_x)\text{O}_{10}(\text{OH})_2$	Al^{3+}		$0 \leq x \leq 0.27$	
Synthetic	$\text{Si}_4(\text{Mg}_{3-x}\text{R}_x)\text{O}_{10}(\text{OH})_2$	Zn	7	$0 \leq x \leq 3$	This study
		Ni	7	$0 \leq x \leq 3$	
		Co	1	$x = 3$	
$\text{Ge}_4(\text{Mg}_{3-x}\text{R}_x)\text{O}_{10}(\text{OH})_2$		Mg	1	$x = 0$	Martin et al. (1992, 1996)
		Ni	1	$x = 3$	
		Co	1	$x = 3$	

octahedral environments. Furthermore, talcs with various chemical compositions can be easily synthesized (e.g. Wilkins and Ito 1967; Petit 2004).

Materials and methods

The talc samples are described in the Table 1. Those containing octahedral Al and Fe^{2+} are natural, and their geological origin, together with their detailed crystal chemistry, is given by Petit et al. (2004). The other samples are synthetic. Talc samples of the solid solutions between the Mg–Si end member and Ni^{2+} -, Co^{2+} - and Zn^{2+} -Si end members were hydrothermally synthesized at 200 °C following procedures outlined by Decarreau et al. (1989). In addition, the Ni^{2+} -, Co^{2+} - and Mg^{2+} -Ge talcs synthesized by Martin et al. (1992, 1996) were used.

The KGa-1 and SAz-1 from the Clay Mineral Society Source Clays were chosen as reference samples of kaolinite and montmorillonite, respectively. The Li-treated SAz-1 sample was obtained after Li^+ saturation and 200 °C overnight heating. The thermal treatment of octahedrally charged smectites (i.e. montmorillonites), saturated with small cations such as Li^+ , reduces their negative layer charge due to migration of the small cation into the vacant octahedral site (Madejová et al. 2000b). This phenomenon is well known as the Hofman-Klemen effect (Hofman and Klemen 1950). A dickite sample from Nowa Ruda (Poland) and a nacrite sample from Lodève (France) described by Buatier et al. (1996) were also analyzed.

A Nicolet 510 FTIR spectrometer was employed to record FTIR spectra at 4-cm^{-1} resolution in the $4000\text{--}400\text{ cm}^{-1}$ range (MIR region). The spectrometer was continuously purged with dry air during scanning of the transmission spectra. The KBr pellets, 2 cm in diameter, were prepared by mixing 3 mg of sample with 300 mg of KBr and heated overnight at 110 °C to remove absorbed water.

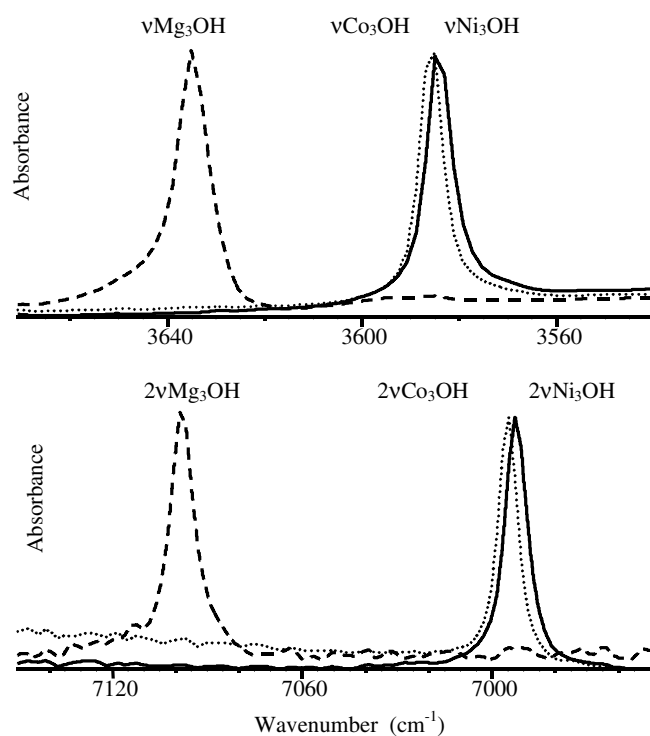


Fig. 1 FTIR spectra in the νOH (top) and $2\nu\text{OH}$ regions (bottom) of synthetic Mg-, Ni-, Co-Ge talcs

NIR spectra were obtained using a Nicolet Magna 760 FTIR spectrometer with a diffuse reflectance (DRIFT) accessory Collector from Spectra-Tech. The spectrometer was equipped with a CaF_2 beam splitter and a PbSe detector. Powder samples were analyzed without any dilution in the KBr matrix. For each sample, 128 scans were recorded in the $11\,000\text{--}4000\text{-cm}^{-1}$ spectral range with a resolution of 4 cm^{-1} . The DRIFT technique is especially appropriate in the NIR region where, in contrast to the MIR region, no dilution of the sample is necessary and therefore its analysis can be very fast and non-destructive.

The Kaleidagraph software was used for the quantitative comparison of the curve fits giving the chi square (χ^2) and correlation coefficient (R^2) values.

Results

Establishment of the relation

Talc is a 2:1 trioctahedral layer silicate. In talc, the OH point perpendicularly toward the hexagonal cavity and are linked to three octahedral cations. The characteristics (electronegativity, atomic mass, cation size, etc.) of these three cations induce specific wavenumbers of the vibrations of the OH groups. The νOH and $2\nu\text{OH}$ regions of the infrared spectra of talc look similar and reveal either one (Fig. 1) or several (Fig. 2) narrow

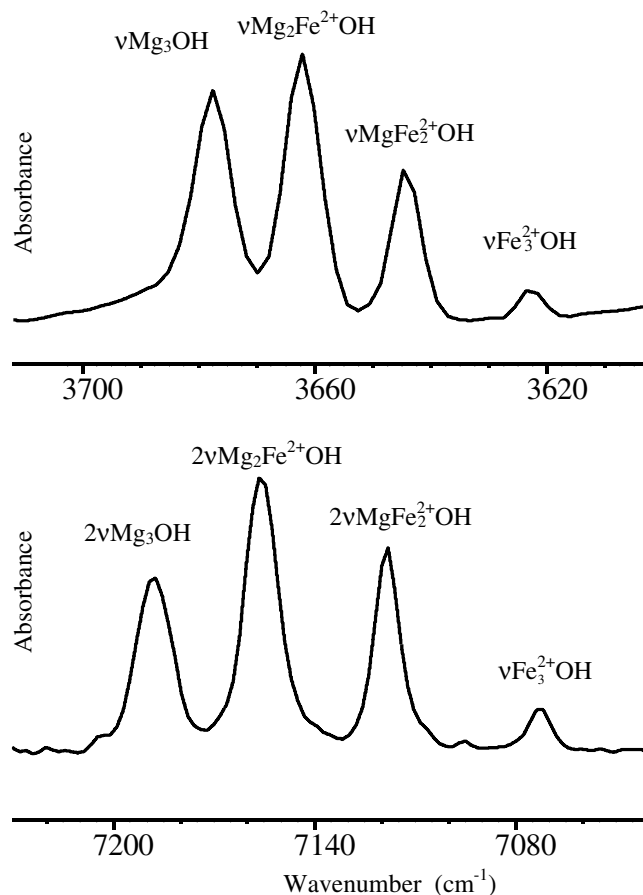


Fig. 2 FTIR spectra in the νOH (top) and $2\nu\text{OH}$ regions (bottom) of the natural iron-rich talc from Antwerp

Table 2 Wavenumbers (in cm^{-1}) of the νOH and $2\nu\text{OH}$ bands observed for various octahedral and tetrahedral environments in natural and synthetic talcs, and calculated values of the anharmonicity constant X

Octahedral group	$W_{\nu\text{OH}}$	$W_{2\nu\text{OH}}$	X
Mg_3	3677	7185	-84.5
Mg_2Ni	3661	7154	-84
MgNi_2	3647	7122	-86
Ni_3	3627	7080	-87
Mg_2Fe	3662	7156	-84
MgFe_2	3644	7118	-85
Fe^{2+}_3	3623	7073	-86.5
Co_3	3631	7087	-87.5
Mg_2Zn	3667	7165	-84.5
MgZn_2	3655	7139	-85.5
Zn_3	3641	7112	-85
Mg_2Al	3652	7136	-84
$(\text{Ge}^{\text{IV}})_3$	3635	7098	-86
$(\text{Ge}^{\text{IV}})_2\text{Ni}$	3584	6993	-87.5
$(\text{Ge}^{\text{IV}})_2\text{Co}$	3586	6995	-88.5

bands depending on the talc crystal chemistry. For talcs from binary octahedral solid solutions, up to four peaks associated with OH vibrations can be distinguished, corresponding to the four possible combinations of the two different cations within three octahedral sites that are directly linked to an OH group (Fig. 2). The assignment of νOH bands to specific octahedral groups is then relatively easy in talc, and published data are available (Wilkins and Ito 1967). The position in wavenumbers for the fundamentals bands ($W_{\nu\text{OH}}$) measured for various octahedral groups in talcs are reported in Table 2 and are in accordance with published data (Wilkins and Ito 1967). Because spectra in both NIR and MIR regions are very similar (Figs. 1 and 2), the $2\nu\text{OH}$ bands are attributed analogously to the νOH bands.

The anharmonicity constant X , which depends on the nature of the oscillator and which may be affected by the OH environment (formation of hydrogen bonds, intermolecular interactions etc.) is calculated by the following equation (Bourd eron and S andorfy 1973; S andorfy 1995; Stefov et al. 2000):

$$X = W_{2\nu\text{OH}}/2 - W_{\nu\text{OH}}, \quad (1)$$

where $W_{2\nu\text{OH}}$ and $W_{\nu\text{OH}}$ are the wavenumbers of the fundamental OH and of the first overtone, respectively. The values of the anharmonicity constant were calculated from the wavenumbers of the fundamental OH and of the first overtone for the same OH group (Table 2). These values of anharmonicity constant are very similar ($-86 \pm 2.5 \text{ cm}^{-1}$) whatever the octahedral or tetrahedral environment, and are close to those of stretching vibrations of alcoholic OH (-80 cm^{-1} ; Bourd eron and S andorfy 1973). For comparison, the anharmonicity constants for the OH symmetrical and antisymmetrical stretching vibrations of water are, respectively, 44 and 46 cm^{-1} (Darling and Dennison 1940).

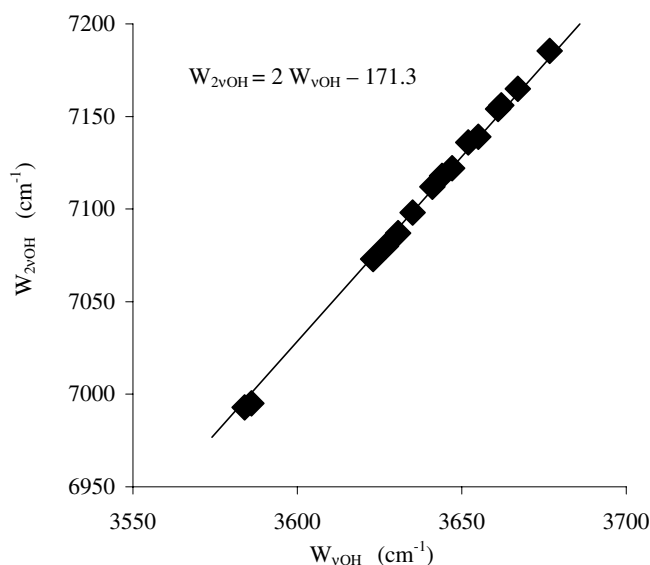


Fig. 3 Wavenumbers of the νOH bands versus wavenumbers of the $2\nu\text{OH}$ bands for various OH groups in talcs (see Table 2). The size of symbol denotes the error on the wavenumber measurements

The wavenumbers of both the νOH and $2\nu\text{OH}$ bands for the same OH groups (Table 2) were plotted, and a clear linear relationship is evidenced (Fig. 3), due to the similar values of anharmonicity constant measured.

From Eq. (1), the relation between $W_{2\nu\text{OH}}$ and $W_{\nu\text{OH}}$ is:

$$W_{2\nu\text{OH}} = 2W_{\nu\text{OH}} - k \text{ cm}^{-1}, \quad (2)$$

where $W_{2\nu\text{OH}}$ is the wavenumber of the first overtone, $k = -2X$, and $W_{\nu\text{OH}}$ is the wavenumber of the fundamental OH band.

Following Eq. (2), our experimental data are best fitted with k equal to 171.27 cm^{-1} (Table 3). This value is very close to the values of 176 and 168 cm^{-1} , respectively, estimated by Frost et al. (2001) and Madejov a et al. (2000a) from the vibrations of the internal OH of kaolinite and of the AlMgLiOH groups in Li-treated montmorillonites, respectively. The values for k of more than 200 cm^{-1} obtained by Frost et al. (2001) for the other νOH bands of kaolinite (inner-surface OH) are far higher (see the quantitative comparison given in Table 3). On the other hand, the method of Bishop et al. (2002b), where $W_{\nu\text{OH}}$ was multiplied by a factor of 1.96, is approximate, and always overestimates the $W_{2\nu\text{OH}}$ by a value of at least 20 cm^{-1} .

Table 3 Parameters of the linear curve fits ($W_{2\nu\text{OH}} = aW_{\nu\text{OH}} - k$) of the plot (see text)

	a	k	χ^2	R^2
This work	2	171.27	119	0.997
Madejov�a et al. (2000a)	2	168	279	0.993
Frost et al. (2001)	2	176	454	0.990
Bishop et al. (2002b)	1.96	0	10 119	0.771

From our experimental data, the anharmonicity constant X can be assumed to be -85.6 cm^{-1} for all the OH-stretching vibrations in talc.

Applications

The interest of the relation established above from talc between $W_{\nu\text{OH}}$ and $W_{2\nu\text{OH}}$ can be applied to other phyllosilicates, at least for the OH vibrations whose OH are from the octahedral sheet and weakly hydrogen-bonded. The idea is to transpose the wide knowledge and databases available on the fundamental νOH bands into the first overtones region where only few interpretative data exist. As shown in Fig. 1, for talc, it is straightforward to assign the $2\nu\text{OH}$ bands in the NIR region knowing the νOH ones, because the analogy between both MIR and NIR regions is obvious (same shape and number of bands). However, for other clay minerals exhibiting more complex spectra, a relation is needed to interpret more easily the NIR region, by locating the first overtone knowing the fundamental absorption band. Some examples follow.

Smectite is, as talc, a 2:1 phyllosilicate. However, heterovalent substitutions cause an overall negative charge on the layers, which is compensated by hydrated

Table 4 Comparison between the observed $W_{\nu\text{OH}}$ for SAZ-1 montmorillonite and the $W_{\nu\text{OH}}$ calculated from Eq. (2) and from the measured $W_{2\nu\text{OH}}$

	$W_{2\nu\text{OH}}$ observed	$W_{\nu\text{OH}}$ calculated	$W_{\nu\text{OH}}$ observed
SAZ-1	7058	3615	3622
Li-treated SAZ-1	7109 7172	3640 3672	3638 3670

interlayer cations. The νOH absorption bands of smectite are generally broader than those of talc mainly due to less crystalline order and to overlapping of structural OH and water bands. Sharper OH bands appear in montmorillonite IR spectra after Li-treatment, due to Li migration into the octahedral vacant site which creates local trioctahedral environments (Madejová et al. 2000a, b). For example, relatively sharp bands appear at 7172 and 3670 cm^{-1} in the Li-treated SAZ-1 montmorillonite (Fig. 4). For SAZ-1 montmorillonite, the $W_{\nu\text{OH}}$ calculated using Eq. (2) from measured $W_{2\nu\text{OH}}$ (at the top of the bands) correspond relatively well to the ones measured for the Li-treated sample (Table 4). For the untreated montmorillonite, bands are broader (not shown), and the difference between calculated and observed $W_{\nu\text{OH}}$ is higher ($\pm 7 \text{ cm}^{-1}$). This is due to the complexity of the observed band, which is, in fact, composed of several overlapping bands corresponding to several OH groups (Al_2OH , AlMgOH etc.) and to water. If the elementary bands due to structural OH in the NIR and MIR regions are linked by the relation determined above (Eq. 2), depending on the proportions and the positions of these elementary components, the maximum of the resulting complex bands in the NIR and MIR regions are not necessarily linked by this relation. If the Eq. (2) is suited to the maximum of the complex broad band of the Li-treated montmorillonite (at 3638 and 7109 cm^{-1} , Table 4), it is probably because the maximum of the complex broad band corresponds to the maximum of an outstanding elementary component.

For kaolinite, which is a 1:1 layer silicate, the OH vibrations bands are sharp, but the complete assignment of these bands is still in dispute. Kaolinite contains four OH groups labelled OH(1 to 4) after Bish's (1993) notation, OH(1) corresponds to the internal OH lying almost in the (001) plane, while the other three correspond to the inner-surface hydroxyls and are inclined at angles of $60\text{--}73^\circ$ to the (001) plane. In the MIR spectra of kaolinite, the $\nu\text{Al}_2\text{OH}$ bands were observed at 3694, 3669, 3652 and 3619 cm^{-1} (Fig. 5). Note that the measured positions of the bands are not obtained by decomposition, and correspond to the maximum height of the peak observed. The 3619- cm^{-1} band is attributed to OH(1). The three other bands are more controversially attributed. Some authors assigned the 3694, 3669 and 3652 cm^{-1} bands to individual OH oscillators, i.e. to OH(3), OH(4) and OH(2), respectively (Shoval et al. 2002). Other studies suggest that the three inner-surface hydroxyls couple to give two weak out-of-phase

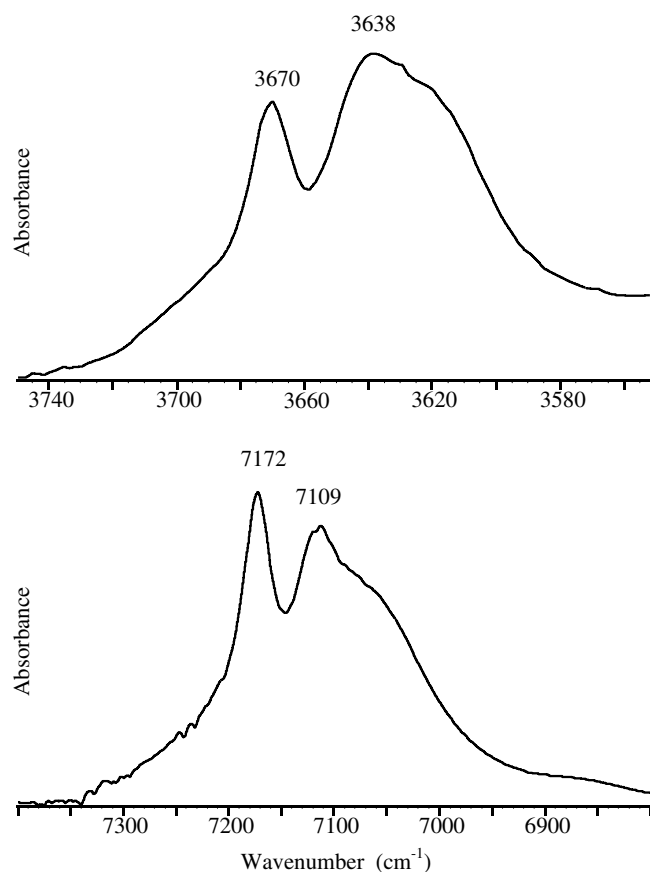


Fig. 4 FTIR spectra in the νOH (top) and $2\nu\text{OH}$ regions (bottom) of the SAZ-1 montmorillonite (Li-treated)

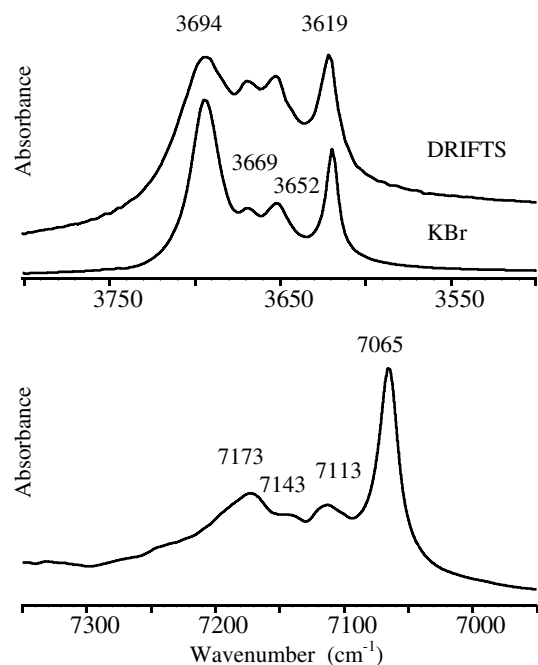


Fig. 5 FTIR spectra in the νOH (top) and $2\nu\text{OH}$ regions (bottom) of the KGa-1 kaolinite

vibrations at 3669 and 3652 cm^{-1} , and a strong in-phase symmetric stretching vibration at the higher wavenumber (Prost et al. 1987; Farmer 1998, 2000; Frost and Klopogge 2001).

In the 7000- cm^{-1} region, four bands were also observed at 7173, 7143, 7113 and 7065 cm^{-1} (Fig. 5). The relative intensities of the four bands clearly vary between the NIR and the MIR region, notably the intensity of the 7173 cm^{-1} band is relatively lower than that of the 7065 cm^{-1} one in the NIR compared to the MIR (Fig. 5). It has been suggested that pressing kaolinite particles when making KBr pellets had an effect on the intensities of the νOH bands (Bell et al. 1991). However, the changes in relative intensities are also observed using the same DRIFTS technique when recording NIR and MIR spectra (Fig. 5). This may reflect coupling between vibrations and Fermi resonance affecting the intensities in the NIR and MIR range differently (Herzberg 1945). Alternatively, formation of hydrogen bonds with OH groups may alter the relative ratio of intensities of the OH bands in the NIR and MIR regions, as in the case of alcohols (Sándorfy 1995).

For kaolinite, the $W_{\nu\text{OH}}$ calculated from measured $W_{2\nu\text{OH}}$ using Eq. (2) are compared with the measured ones (Table 5). For the 7173-, 7143- and 7065- cm^{-1} bands, a relatively good agreement ($\pm 5 \text{ cm}^{-1}$) is obtained between the calculated and observed $W_{\nu\text{OH}}$, meaning that these bands are mainly due to the first overtones of the 3669-, 3652- and 3619- cm^{-1} bands. However, the 7113- cm^{-1} band does not correspond to an observable νOH band, and the intense 3694- cm^{-1} band corresponds only to a very broad shoulder located near 7220 cm^{-1} (Fig. 5). Major NIR spectral features of kaolinite are located in the

Table 5 Comparison between the calculated and observed $W_{\nu\text{OH}}$ and $W_{2\nu\text{OH}}$ for kaolinite (KGa-1), dickite (Nowa Ruda, Poland) and nacrite (Lodève, France). (a) using Eq. (2); (b) using Eq. (3)

	$W_{2\nu\text{OH}}$ observed	$W_{\nu\text{OH}}$ calculated	$W_{\nu\text{OH}}$ observed	$W_{2\nu\text{OH}}$ calculated
		(a)		(b)
Kaolinite				
			3694 ^A	7217 ^{A+A}
	7173	3672	3669 ^B	7192 ^{A+B}
	7143	3657	3652 ^C	7175 ^{A+C}
	7113	3642		7167 ^{B+B}
	7065	3618	3619 ^D	7150 ^{B+C}
				7142 ^{A+D}
				7133 ^{C+C}
				7117 ^{B+D}
				7100 ^{C+D}
				7067 ^{D+D}
Dickite	7240	3706	3704	7237
			3654	7137
	7070	3621	3621	7071
Nacrite	7230	3701	3700	7229
			3648	7125
	7086	3629	3629	7087

5000–4000- cm^{-1} and 7000- cm^{-1} regions (Petit et al. 1999). The former is the ($\nu\text{OH} + \delta\text{OH}$) combination band region, while the latter is the νOH first overtone region. One can assume that combinations of any νOH bands would occur in overlapping of the first overtones in the 7000- cm^{-1} region. Hypothesizing that the anharmonicity constant does not vary a lot between the $2\nu\text{OH}$ first overtones and the $2\nu\text{OH}$ combination bands, the $W_{2\nu\text{OH}}$ are calculated using the following equation derived from Eq. (2), and combining any two of the observed $\nu\text{Al}_2\text{OH}$ band:

$$W_{\nu\text{OH}(x+y)} = W_{\nu\text{OH}x} + W_{\nu\text{OH}y} - 171 \text{ cm}^{-1}, \quad (3)$$

$\nu\text{OH}x$ and $\nu\text{OH}y$ being $\nu\text{Al}_2\text{OH}$ bands. The calculated $W_{2\nu\text{OH}}$ values are given in Table 5. The occurrence of several bands in the high wavenumber side ($> 7167 \text{ cm}^{-1}$) accounts well for the shape of the spectra in the $2\nu\text{OH}$ region, where several bands probably overlap (Fig. 5). Moreover, the combination of the 3619- and 3669- cm^{-1} bands accounts well for the 7113- cm^{-1} value (Table 5).

The other kaolinite polymorphs, dickite and nacrite, show two $2\nu\text{Al}_2\text{OH}$ (Table 5) in accordance with Pontual et al. (1997), while three $\nu\text{Al}_2\text{OH}$ bands are observed (Table 5) in accordance with Prost et al. (1987). From the position of the two bands observed in the NIR, Eq. (2) allows the position of two of the three bands observed in the MIR spectra to be calculated with good precision ($\pm 2 \text{ cm}^{-1}$) (Table 5), suggesting that the 7240- and 7070- cm^{-1} bands for dickite and the 7230- and 7086- cm^{-1} bands for nacrite are due to the first overtones of the 3704- and 3621- cm^{-1} bands for dickite, as well as the 3700- and 3629- cm^{-1} bands in nacrite. The first overtones of the 3654- cm^{-1} band for dickite and the 3648- cm^{-1} band for nacrite do not occur or are too weak to be observed.

Discussion

Talc samples with various crystal chemistries were used to establish a relation between fundamentals (νOH) and

first overtones ($2\nu_{\text{OH}}$) of vibrations of structural OH groups in clay minerals. A perfect linear relation was found between the wavenumbers of the fundamentals and the first overtones, making it possible to switch easily from $W_{2\nu_{\text{OH}}}$ in NIR to $W_{\nu_{\text{OH}}}$ in MIR for structural OH groups in talcs. It is shown that this relation, established from talc samples because their absorption bands are narrow, and because their range of OH vibrations wavenumbers are wide, can be used for any other clay minerals, at least for the OH vibrations whose OH are from the octahedral sheet and similarly hydrogen-bonded, such as smectite and kaolinite. The experimental data are well fitted with Eq. (2) based on this theory. The value of the anharmonicity constant of the stretching vibrations of the OH groups experimentally determined is -85.6 cm^{-1} . As far as the authors are aware, it is the first time that the value of the anharmonicity constant of the OH-stretching vibrations is determined for phyllosilicates.

The relationship established above between $W_{2\nu_{\text{OH}}}$ and $W_{\nu_{\text{OH}}}$ allows us to utilize the wide knowledge on the nearest OH group cationic environments and the corresponding $W_{\nu_{\text{OH}}}$ available in MIR for the interpretation of the OH overtone in the NIR region. Compared to IR spectroscopy in the MIR region, NIR spectroscopy is easier to use (no preparation of samples), completely non-destructive, fast and with a higher sensitivity to the OH group environment. Our findings show clearly the efficiency of FTIR measurements on clay minerals using both MIR and NIR spectra. Nevertheless, the whole understanding of the origin of observed absorption bands needs a more quantitative approach and/or complementary studies using ab initio computations (e.g. Balan et al. 2001). It is worth noting that one could also treat the regions of the first overtones and combination vibrations of the OH group separately and apply the relations developed by Besson and Drits (1997a, b) and Gates (2004). However, this treatment would require that considerable details about the chemistries of the samples would already be known. Thus, the relationship given in Eq. (2) can be generally applied to better discriminate the presence of distinct types of clay minerals.

The interpretation work in NIR is also important for the field geology. Spectral analysis with the field spectrometer is commonly used to discriminate compositional variations within mineral groups, which is significant, as mineral composition may vary systematically in an alteration system as a function of the temperature and composition of the altering fluids and with proximity to zones of mineralisation. Mapping these variations can allow the field geologists to define mineralization/alteration relationships and to position samples within an alteration system (Pontual and Cocks 1994). Accurate interpretations of spectra could contribute to a more precise quantitative analysis of clay minerals and to a better understanding of their mineralization/alteration relationships.

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