EXPERIMENTALLY DETERMINED RELATIONSHIP BETWEEN WAVENUMBER OF vOH STRETCHING VIBRATIONS AND THEIR FIRST OVERTONES FOR CLAYS*

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Historically, the near infrared (NIR) and middle infrared (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. Some mineralogical data for clays and clay minerals in the NIR are available (e.g. Hunt and Salisbury, 1970), mainly because field and imaging spectrometers, and hyperspectral remote sensing work exclusively in the NIR (and visible) region.

Recent results of the NIR region for analysing the crystal chemistry of clay minerals have significantly extended the application of this spectroscopy. 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 a) isomorphous substitutions in talcs (Petit et al., 2004) and nontronites (Gates et al., 2002); b) fixed Li in reduced-charge montmorillonites (Madejová et al., 2000); c) Si-OH groups in acid-treated smectites (Pálková et al., 2003). Another utility of NIR region is to recalculate the positions of the OH vibrational bands in MIR as shown by Petit et al. (1999) for the $\delta AlGaOH$ and $\delta AlCrOH$ bands in MIR spectra of Ga- and Cr-bearing kaolinites.

The observed bands in the NIR first overtone region are commonly assigned by analogy with the MIR vOH region. However, to interpret spectra, researchers often need a relationship which allows them to calculate the wavenumbers of the first overtone (2vOH) in the NIR from the wavenumbers of the fundamental (vOH) in the MIR and vice versa (e.g. Bishop et al., 2002; Frost et al., 2001).

The aim of this work is to determine a relationship between the wavenumbers of the first OH stretching overtones (W_{2vOH}) and the wavenumbers of the OH stretching fundamentals (W_{vOH}) to help to interpret the near infrared spectra of clay minerals. 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 that of the fundamental bands (e.g. Herzberg, 1945), and X the anharmonicity constant is defined by the following relation:
$$X = W_{2vOH} / 2 - W_{vOH}.$$

To derive the basic correlation between the vOH and 2vOH wavenumbers, the selected samples are talcs because their absorption bands are narrow, with few overlapping peaks if any, and they are sensitive to a variety of octahedral environments. Furthermore, talcs with various chemical compositions can be easily synthesised.

It is shown that the anharmonicity constant X remains almost unchanged for several types of clay samples. Therefore the relation, established from talcs can be used for other clays.

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