Low-temperature infrared spectroscopic study of OH-stretching modes in kaolinite and dickite

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ABSTRACT

The powder-transmission infrared spectra of OH-stretching modes in well-ordered samples of kaolinite and dickite are recorded from 270 to 10 K. Effective medium modeling of the kaolinite spectrum confirms the coupled motion of non-equivalent OH groups in the inter-layer OH-stretching modes. A full assignment of OH-stretching bands in dickite is proposed. In particular, the band observed at 3685 cm⁻¹ in room-temperature spectra is attributed to a kaolinite-like defect, whereas that at 3706 cm⁻¹ is related to OH3 groups of the dickite structure. The changes in phonon frequency and line shape are analyzed as a function of temperature. The results evidence the quasi-harmonic nature of the OH-stretching modes in kaolinite-group minerals. Coupling of OH-stretching modes to each other can be related to the macroscopic electrostatic properties of the composite medium, made of mineral particles and KBr matrix, and not to microscopic anharmonic mechanisms. The low saturation temperatures of vibrational frequencies and linewidths indicate that the OH-stretching modes probe the average thermal bath of the crystal, without coupling to a specific decay channel.

Keywords: Infrared spectroscopy, kaolinite, dickite, thermodynamic, phonons

INTRODUCTION

The stretching vibrational modes of OH groups are commonly used to probe the structural order of hydrous minerals (Farmer 1974). They are sensitive to the occurrence of defects such as cationic substitutions and planar defects, and to the structural changes associated with phase transitions. This is particularly true for hydrous layered minerals, such as kaolinite group minerals, serpentines, or aluminum hydroxides that display significant modifications under pressure (e.g., Johnston et al. 2002). These minerals also display a great variability of their defective structure that can be used to gain information about the physical-chemical conditions that prevailed during their formation (Muller et al. 1995). In particular, infrared spectroscopy of OH-stretching modes has been used to unravel the transformation of kaolinite group minerals in natural environments (e.g., Beaufort et al. 1998; Balan et al. 2007a) and can be applied to optimize the use of kaolin-based materials (e.g., Fourdrin et al. 2009). It has also been shown that the narrowing and differential shift of OH-stretching infrared absorption bands at low temperature can be used to improve the identification of stacking faults in disordered varieties of kaolinite-group minerals (Prost et al. 1989; Brindley et al. 1986; Bish and Johnston 1993; Johnston et al. 2008). In addition, the high quality of some kaolinite-group mineral samples together with the relatively small size of their unit cell make them important model compounds to investigate the bulk and surface properties of hydrous minerals by theory and experiment (Geysermans and Noguera 2009).

The OH-stretching modes are usually considered as significantly anharmonic (e.g., Tosoni et al. 2005; Prencipe et al. 2009). However, first-principles harmonic calculations in hydrous, layered minerals contradict this view and have provided a description of OH-stretching vibrations, which is fully consistent with experiment (e.g., Balan et al. 2001, 2002a, 2005, 2006). In fact, previous investigations of anharmonicity in hydrous minerals mostly focused on the frequency shift observed between harmonic and anharmonic calculations. From an experimental point of view, the shift can be assessed by comparing the frequency of fundamental and overtone bands (Petit et al. 2004) or by analyzing the frequency changes induced by D/H isotopic substitution (Berglund et al. 1978). Perturbation theory applied to OH-stretching modes evidences that the large frequency shift mostly results from the small effective mass of the stretching modes related to the small mass of hydrogen; whereas the potential energy profile associated with stretching modes is only very weakly anharmonic (Balan et al. 2007b). In this article, we re-examine the anharmonic character of OH-stretching modes in kaolinite and dickite, the most common polymorphs of aluminous phyllosilicates, by analyzing the changes in phonon frequency and line shape as a function of temperature. Our results evidence the quasi-harmonic nature of the OH-stretching modes in these kaolinite-group minerals and provide an interpretation for all OH-stretching absorption bands observed in the infrared spectrum of kaolinite and dickite.

EXPERIMENTAL MODES

Infrared spectra were recorded on well-ordered samples of kaolinite (GB1) from St. Austell (Great Britain) (Cases et al. 1982; Balan et al. 2000) and dickite (S1) from El Berrocal, Spain (Allard et al. 2003; Balan et al. 2005). Additional