The vibrational spectrum of lizardite-1T [Mg$_5$Si$_4$O$_{10}$(OH)$_4$] at the Γ point: A contribution from an ab initio periodic B3LYP calculation

MAURO PRENCIPE, 1,* YVES NOEL, 2 MARCO BRUNO, 1 AND ROBERTO DOVESI 3

1 Dipartimento di Scienze Mineralogiche e Petroligiche, Università di Torino, Via Valperga Caluso 35, 10125 Torino, Italy
2 Laboratoire de Pétrologie, Modélisation de Matériaux et Processus, Université Pierre et Marie Curie, 4, Place Jussieu, 75232 Paris cedex 05, France
3 Dipartimento di Chimica IFM e NIS-Centre of excellence, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy

ABSTRACT

The vibrational spectrum of lizardite at the Γ point has been calculated with ab initio methods, using a hybrid HF/DFT Hamiltonian (B3LYP). Apart from a few bending modes involving hydrogen motion, very good agreement has been found between calculated and experimental infrared and Raman spectra of the mineral. The anharmonic correction to the OH-stretching modes proved to be crucial for a correct evaluation of their frequencies and, on average, it amounts to a lowering of about 150 cm$^{-1}$ with respect to the values computed within the harmonic approximation. LO-TO splitting effects had to be taken into account for a correct interpretation of the data obtained from infrared spectra on powder samples. The calculation can be used either to confidently identify which bands in the experimental spectra do correspond to fundamental vibrational transitions or to unequivocally assign them to specific normal modes.

Keywords: Lizardite, vibrational frequencies, normal modes, computational modeling

INTRODUCTION

Lizardite-1T [ideal formula Mg$_5$Si$_4$O$_{10}$(OH)$_4$, space group $P31\text{m}$] is a layer silicate belonging to the serpentine family of minerals (Mellini and Viti 1994). It consists of silicate tetrahedral sheets and brucite-like magnesium octahedral sheets, which alternate along [001] (see Fig. 1). The study of the vibrational properties of lizardite is particularly important in view of the direct application to the recognition, by means of IR and Raman spectroscopies, of the presence of asbestos (chrysotile, in particular) with which lizardite is often associated, in various manufactured or natural materials. The interpretation of the experimental vibrational spectra (Auzende et al. 2004; Balan et al. 2002; Fuchs et al. 1998; Hofmeister and Bowey 2006; Post and Borer 2000; Rinaudo et al. 2003) can be complicated by several factors, among which are: (1) the presence of impurities in the natural samples; (2) the nature and morphology of the samples (usually powders) that affect the possible observation of LO modes having relatively high intensities; (3) the presence in the spectra of overtones and/or combination bands; (4) failure to observe modes associated with low transition moments; and (5) band broadening producing extensive band overlap. Even after a successful identification of all of the fundamental vibrational transitions, a problem exists concerning their assignment to specific normal modes; in general such problems cannot reliably be solved without the simulation of the vibrational spectrum by some theoretical ab initio or empirical calculation. The method used in the present work has proved to be particularly effective in the ab initio calculation of vibrational spectra of minerals (Demichelis et al. 2007; Orlando et al. 2006; Pascale et al. 2004a, 2004b, 2005a, 2005b; Prencipe et al. 2004, 2006; Tosoni et al. 2006; Ugliengo et al. 2004; Valenzano et al. 2007), and it was thus used in our study of lizardite.

The importance has been emphasized of a correct evaluation of the LO-TO splitting effects and their impact on the experimental infrared spectra collected on powder samples having crystallites showing a plate-like particle morphology (Balan et al. 2001, 2002; Farmer and Russell 1964, 1966; Farmer 1998, 2000; Gonze and Lee 1997). From a computational point of view, the importance of anharmonic effects on the OH-stretching modes, and the role of the Hamiltonian in providing frequencies in agreement with the experimental measurements are also discussed; in particular, the performances of the hybrid HF/DFT B3LYP Hamiltonian (Becke 1993), containing a fraction of the exact non local Hartree-Fock exchange, and that of a purely DFT Hamiltonian (PBE; Perdew et al. 1996), used in a previous work on lizardite (Balan et al. 2002) are compared. It is to be noted that in the work by Balan et al. (2002) no account was given for the relatively strong anharmonic effects on the frequencies of the OH-stretching vibrations.

COMPUTATIONAL DETAILS

Geometry optimization and calculations of spectra were performed by means of the ab initio CRYSTAL06 code (Dovesi et al. 2006), which implements the Hartree-Fock and Kohn-Sham, self-consistent field (SCF) method for the study of periodic systems (Pisani et al. 1988), by using a Gaussian type basis set.

Basis set

The basis set consisted of an 85-11G* contraction for Mg (Valenzano et al. 2007; the star indicates the presence of $d$ functions), 88-31G* and 8-411G* contractions for Si and O, respectively.