Combined inelastic neutron scattering and solid-state density functional theory study of dynamics of hydrogen atoms in muscovite 2\(M_1\)

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ABSTRACT

Inelastic neutron scattering (INS) was used to study dynamics of the hydrogen atoms in natural 2\(M_1\) muscovite in the 150–1200 cm\(^{-1}\) energy range. The resultant INS spectra are interpreted by means of solid-state density functional theory calculations covering both normal mode analysis and molecular dynamics. While signatures of the Al-O-H bending modes were found over the whole energy transfer range, the dominant contributions were observed between 800–1000 cm\(^{-1}\). The modes assigned to the in-plane movements of the respective hydrogen atoms are well defined and always appear at high energies. In contrast, the modes corresponding to the out-of-plane movements are spread over large energy transfer ranges, extending down to the region of external (lattice) modes. The positions of the high-energy modes contributing to the INS band at ~907 cm\(^{-1}\) depend on the distance of respective hydrogen atoms to the nearest oxygen atom of the basal net and its polarity.

Keywords: Inelastic neutron scattering, muscovite, DFT, vibrational spectra, molecular dynamics

INTRODUCTION

To elucidate proton dynamics in the 2:1 sheet silicates, we have carried out a combined inelastic neutron scattering and solid-state computational study of the dynamics of the hydrogen atoms in muscovite, a diocathedral 2:1 mica. Protons in micas occupy unique positions, because in the structures of these minerals there are no hydrogen bonds of appreciable strengths, which could significantly confine proton motions. The character of their movements manifested by the corresponding vibrational modes thus reflects, in addition to the bond bending modes, the dynamics of the deformational changes of the polyhedra forming the 2:1 layer as well as the mutual movements of entire 2:1 mica layers. Furthermore, the movements of protons can be influenced by inhomogeneities in their surroundings originating mainly from the chemical variability in the cation positions of the constituting polyhedra. Therefore, the protons can help reveal some fine structural details.

The comprehensive review of Beran (2002) shows that considerable effort has been invested in studying the proton dynamics in micas by conventional IR or Raman spectroscopy, especially within the energy transfer region ~3000–3600 cm\(^{-1}\). This region is the home to the OH stretching modes, which appear uncontaminated by any other vibrational modes. Their unique positions facilitate their measurement, making them a subject of numerous studies. On the other hand, the region of X-O-H (X being Al, Mg, Fe, etc.) deformation modes (~1500 cm\(^{-1}\)) is only rarely examined in the context of proton dynamics because the contributions of the proton containing groups to the optical vibrational spectra are masked by much stronger contributions arising from the motions of heavier atoms (Farmer and Russell 1964).

The use of INS to study proton dynamics has several advantages over the well-established IR or Raman spectroscopy. In particular, hydrogen has by far the largest incoherent neutron scattering cross-section of all elements and thus the signatures of hydrogen motions are the most prominent features of any INS measurement. Furthermore, for INS there are no selection rules that cause several modes to be absent (Dove 2002; Chaplot et al. 2002; Mitchell et al. 2005). Finally, the measured INS intensities are directly proportional to the mean square displacements of the hydrogen atoms in the corresponding modes. Therefore, the standard methods of normal modes analysis (NMA) or Fourier transform power spectra of individual velocity autocorrelation functions obtained by molecular dynamics simulations can be used to model the measurements. The power of the INS as a probe of hydrogen atoms dynamics can be further enhanced by combining it with the predictive capabilities of theoretical methods, in particular of modern solid-state density functional theory (DFT) calculations.

We have recently applied this approach successfully in the INS/DFT studies of hydrogen atoms dynamics in kaolinite-DMSO intercalate and in a highly ordered kaolinite (Smrčok et al. 2010a, 2010b), where not only detailed assignments of the individual vibrational modes were presented, but where also the influence of O-H⋯O hydrogen bonds on the interlayer proton dynamics was documented. An interesting result of both studies was that the modes generated by the protons positioned inside