



## Research paper

# Influence of layer charge, hydration state and cation nature on the collective dynamics of interlayer water in synthetic swelling clay minerals



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## ABSTRACT

The dynamical and structural properties of water in clay interlayers can be considered as those of a bidimensional confined fluid with significant anisotropy as revealed by measurements and simulations of water diffusion at the molecular scale. The present paper investigates water collective motions by using coherent inelastic neutron scattering (INS) on deuterated samples of synthetic saponite samples with low (0.7 per unit cell) and high (1.4 per unit cell) charge, Na<sup>+</sup> and Ca<sup>2+</sup> interlayer cations, various hydration states and at different temperatures. In all cases, two excitations are needed to fit the inelastic signals. The low-energy excitation of the collective dynamics of interlayer water evidences a clear anisotropy and displays a behavior significantly different from that of bulk water, this difference being stronger in the direction perpendicular to the clay layer. In the parallel direction, experimental results and molecular dynamics simulations show that the features of the low-energy excitation and in particular, the energy corresponding to the nondispersive component are linked to the structuration and rigidity of the interlayer water network. Indeed, this position displays an upward energy shift with increasing confinement and decreasing temperature. In contrast, data obtained in the perpendicular direction, display a dispersive behavior for Q values  $\geq 0.5 \text{ \AA}^{-1}$  in contrast with what is observed for bulk water and in the parallel direction. Such a behavior must somehow be linked to a correlation between the motions of water molecules located in adjacent interlayer space that is likely transmitted through the solid clay layer.

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## 1. Introduction

Upon water adsorption, swelling clay minerals expand stepwise. Their apparent interlamellar distance ( $d_{001}$ ) then increases step by step from a value around 10 Å for the dry state to roughly 12.5 Å for the so-called monohydrated state and then to around 15.5 Å for the bihydrated state. The domains of existence of the different hydration states, as well as the exact  $d_{001}$  value, strongly depend on cation nature and on the amount and localization of charges in the TOT layer (e.g., Sato et al., 1992, 1996; Bérend et al., 1995; Cases et al., 1997; Michot et al., 2002, 2005; Ferrage et al., 2005, 2007; Rinnert et al., 2005). In such systems, the dynamical and structural properties of water can be considered as those of a bidimensional confined fluid. Indeed, the system displays strong confinement in the direction perpendicular to the clay layers, inducing a specific structuration of water molecules. This structuration in turn impacts water organization in the parallel direction, and early molecular simulations studies have

revealed that it is significantly different from that of bulk water (e.g., Delville, 1991, 1993; Skipper et al., 1991; Chang et al., 1995, 1997; Boeket et al., 1995; Smith, 1998; Greathouse and Storm, 2002; Marry et al., 2002; Marry and Turq, 2003). Such anisotropic organization is revealed by measurements of water diffusion in swelling clay interlayers at the molecular scale (sometimes combined with simulations) that yield anisotropic diffusion coefficients significantly lower than that of bulk water (e.g., Olejnik and White, 1972; Cebula et al., 1981; Tuck et al., 1984, 1985; Swenson et al., 2000, 2001; Malikova et al., 2005, 2006; Michot et al., 2007, 2012; Bordallo et al., 2008; Marry et al., 2011, 2013; Bowers et al., 2011; Gates et al., 2012; Morrow et al., 2013; Holmboe and Bourg, 2014). Most of these studies rely on the use of neutron-based techniques (Martins et al., 2014) and exploit either the incoherent signal of hydrogenated water by quasi-elastic neutron scattering (QENS) or the collective motions via the density–density correlation (i.e., intermediate scattering function  $F(Q,t)$ ) measured by means of neutron spin-echo (NSE) experiments. In contrast, much less work has been devoted to the investigation of collective motions measured by coherent inelastic neutron scattering (INS) on deuterated samples. In an INS experiment with a deuterated sample,

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the coherent scattering arising from the interference of the waves of different nuclei is measured, and therefore information about density fluctuations is obtained. The study of these collective motions is thus different from both self-motions of individual molecules obtained by incoherent QENS and slow collective motions obtained by NSE (see e.g. Price, 1997; Price et al., 2003; or Martins et al., 2014 for a general overview of the INS and QENS techniques).

In a recent study (Jiménez-Ruiz et al., 2012), we analyzed the INS signal of an oriented synthetic  $\text{Na}^+$ -saturated saponite sample with a layer charge of 0.7 per unit cell in the bihydrated state. We could evidence a clear anisotropy of the low-energy excitation of the collective dynamics of interlayer water that display a behavior significantly different from that of bulk water, this difference being stronger in the direction perpendicular to the clay layer. Molecular dynamics (MD) simulations of the system could reproduce qualitatively the experimental results that could be assigned to the presence of cations in the interlayer space and/or confinement effects. To get a further understanding of the observed features, it is then necessary to vary cation nature, layer charge and hydration state.

In that context, the present study combines INS measurements and MD simulations carried out on the above-mentioned saponite sample under its calcium form in the bihydrated state, together with measurements performed on a  $\text{Na}^+$ -saponite sample with a higher layer charge (1.4 per unit cell) in the monohydrated state. Further insights about water structuration in the interlayer space will also be obtained by studying some of the samples at different temperatures.

## 2. Materials and methods

### 2.1. Experiments

The two samples used in the present study are synthetic saponite samples with general formulae of  $\text{Si}_{7.3}\text{Al}_{0.7}\text{Mg}_6\text{O}_{20}(\text{OH})_4\text{Ca}_{0.35}$  and  $\text{Si}_{6.6}\text{Al}_{1.4}\text{Mg}_6\text{O}_{20}(\text{OH})_4\text{Na}_{1.4}$  that will be referred to as Sap0.7- $\text{Ca}^{2+}$  and Sap1.4- $\text{Na}^+$ , whereas their hydration state will be referred to as either 1 W or 2 W for monohydrated and bihydrated samples, respectively. Details about the synthesis and crystal chemistry of the studied material can be found in Pelletier et al. (2003) or Michot et al. (2005). Oriented clay films of  $\sim 15 \mu\text{m}$  in thickness were prepared by filtration of a clay dispersion and stacked in a square aluminum cell of  $6 \times 4 \times 0.4 \text{ cm}^3$ . The final clay stack of  $\sim 3 \text{ mm}$  thickness was first dried at  $80^\circ\text{C}$  under primary vacuum ( $\sim 10^{-3} \text{ Pa}$ ) and then equilibrated in deuterated water vapor at high relative humidity ( $\approx 90\%$ ) to ensure a full exchange of the initial interlayer water by heavy water. The relative humidity was then adjusted at 79% for the calcium sample and at 23% for the sodium one. Under such conditions, the calcium sample is under a bihydrated form and the sodium sample under a monohydrated state with very

limited hydration heterogeneity (Ferrage et al., 2010, 2011; Michot et al., 2012). The corresponding d-spacings are 15.30 and 12.31 Å for the calcium and sodium sample, respectively. Hydration integrity was checked throughout the whole INS experiment by measuring regularly the static structure factors of the samples.

The INS experiment was carried out on the thermal three-axis spectrometer IN8C, at the High Flux Reactor of the Institut Laue-Langevin (Grenoble, France). Inelastic measurements probe the energy transfer occurring when a neutron beam interacts with the sample. For a beam with initial and final momentum  $\hbar k_i$  and  $\hbar k_f$  and energy  $E_i = \hbar\omega_i$  and  $E_f = \hbar\omega_f$ , the momentum transfer is  $\Delta p = \hbar(k_i - k_f) = \hbar Q$  and the energy transfer  $\Delta E = \hbar(\omega_i - \omega_f) = \hbar\omega$ . These two quantities are linked and can be derived from a three-axis neutron experiment. In such a set-up, information on the excitation spectrum is obtained for a given point Q in reciprocal space, which is achieved by fixing  $k_f$  and adjusting  $k_i$  at each measurement point using the properties of the so-called scattering triangle (Fig. 1).

Depending on the investigated Q-range, the experiment was therefore carried out at different constant final wave-vectors,  $k_f = 4.1 \text{ \AA}^{-1}$  (for  $Q = 0.2 \text{ \AA}^{-1}$ ),  $5 \text{ \AA}^{-1}$  (for  $Q = 0.3, 0.4$  and  $0.5 \text{ \AA}^{-1}$ ), and  $6 \text{ \AA}^{-1}$  (for  $Q = 0.5\text{--}1 \text{ \AA}^{-1}$ ). The energy transfer range is then provided by the conservation laws of both energy and momentum transfer for each Q and  $k_f$ . The energy resolutions measured at the elastic peak position (i.e. when  $E_i = E_f$ ) using vanadium were fitted by a Gaussian function with full width half-maximum (FWHM) values of 1.27, 2.51, and 4.47 meV, respectively. Maximum flux and relatively high resolution in energy transfer were achieved by using a Cu (200) monochromator and a Cu (111) analyzer. With a sample thickness of  $\approx 3 \text{ mm}$ , the measured sample transmission was 85%, and according to the corresponding scattering of 15%, multiple scattering contributions can be safely neglected. The aluminum cell was placed inside a vacuum box, with an air pressure lower than  $10^{-4} \text{ mbar}$ , which minimizes additional scattering from surrounding air. Inelastic scans were then carried out at the requested temperature (controlled by using an ILL-built cryostat sensitive to 0.1 K) for wave vectors between 0.2 and  $1 \text{ \AA}^{-1}$  using two different orientations of Q with regard to the clay layers: parallel ( $Q_{\parallel}$ ) and perpendicular ( $Q_{\perp}$ ). It was previously shown, by analyzing fully dehydrated samples (Jiménez-Ruiz et al., 2012), that the inelastic spectra recorded in the investigated energy range were dominated by signals corresponding to interlayer deuterated water. For each experimental condition, i.e. one Q-value, one  $k_f$  value and one orientation, the spectrum corresponding to the empty cell was measured. It must be pointed out that the experimental energy range reached for each Q-value is different due to the kinematic conditions imposed by the neutron scattering experiment at very low Q-values. In all cases, possible contamination from the direct beam in the frequency edges of the measured spectra could be discarded after careful comparison between

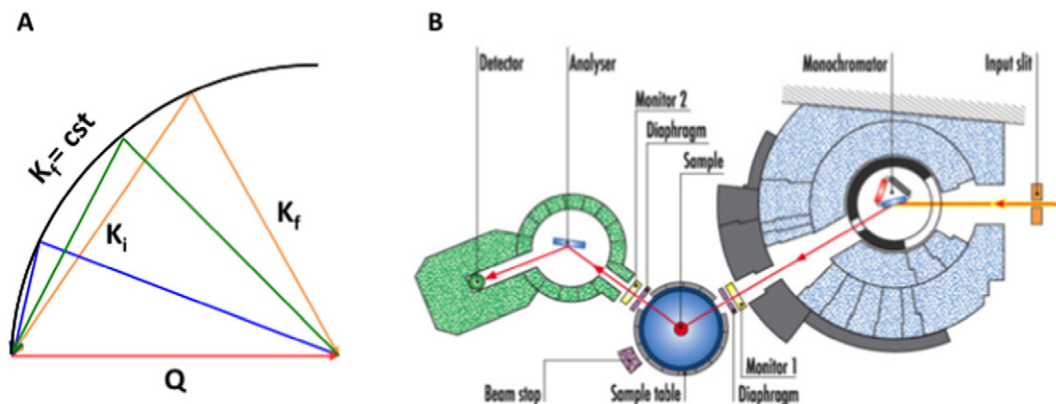


Fig. 1. (A) Principle of a three-axis experiment and (B) scheme of the spectrometer IN8C used in the present study (adapted from the ILL website).

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