CALCULATION OF THE RAMAN SPECTRA OF HYDRATED CLAYS CONTAINING METALS (Zn²⁺ IONS AND WATER IN VERMICULITE)

M. Arab, K. S. Smirnov and D. Bougeard*

Laboratoire de Spectrochimie Infrarouge et Raman, Université de Lille 1, Bât. C5, F-59655 Villeneuve d'Ascq Cedex; E-Mail: Daniel.Bougeard@univ-lille1.fr

Keywords: water, vermiculite, zinc, molecular dynamics

Abstract: The contribution reports the use of vibrational spectra for validation of molecular dynamics calculations and the application of the validated models for the description of the dynamics of water in the interlayer space of clays in the absence and in the presence of metal ions.

A force field derived for aluminosilicates was transferred for the study of the vibrational spectra of kaolinite with the help of molecular dynamics [1]. The same potential model extended by terms taking into account octahedral magnesium permits a good reproduction of the Raman spectrum of vermiculite clay (Fig.1), including the intensities derived from electro-optical parameters. The use of symmetry coordinates of sub-units yields a complete interpretation of the Raman spectrum.



Fig. 1 Experimental (a) and calculated (b) Raman spectra of vermiculite [2]

A similar approach was applied to the modeling of hydrated vermiculite structures without and with Zn^{2+} cations in the interlayer space. In a first step the structure and dynamics of Zn^{2+} in water are described and the Raman spectrum of the octahedral first shell of solvation (Fig. 2) is correctly reproduced. It turns out that the six water molecules reside in the shell for a time longer than the 1 ns length of the MD calculations. The second hydration shell contains about 12.5 molecules with a mean residence time of 7.3 ps [3]. In a second step the structure and dynamics of the interlayer water in a neutral vermiculite-like structure was studied. The MD calculations show the formation of water layers near the clay surface. The interlayer water molecules have a diffusion coefficient (9.2 10^{-10} m² sec⁻¹) about four times smaller than in bulk water (3.9 10^{-9} m² sec⁻¹) [5].



Wavenumber (cm⁻¹) Fig. 2 Calculated Raman spectrum of the $Zn(H_2O)_6^{2+}$ octahedron in the assumption of rigid H₂O molecules (The dashed experimental curve corresponds to a zinc perchlorate solution characterized by the 463 cm⁻¹ band due to the ClO₄⁻ anion [4]

In Zn-vermiculite two types of interlayer water molecules can be identified [6]. The first type is the molecules of the first solvation shell and the second one is the remaining water. The first hydration shell built around the cation has a structure very similar to the octahedron in solution and is stable over the 2.4 ns of the simulation. The second hydration shell consists of 9.2 molecules with a mean residence time of 28.4 ps. The calculated diffusion coefficient of the "bound" and "free" molecules is equal to 2.6 10^{-10} m² sec⁻¹ and 9.1 10^{-10} m² sec⁻¹, respectively. Both values are of the same order of magnitude as the diffusion coefficient measured experimentally.



Fig. 3 Density of vibrational states of the various systems considered in this work

The spectra gathered for all systems in Fig. 3 could be interpreted in terms of structure and dynamics of the water molecules and of the nature and evolution of the hydrogen bond network.

References:

- 1. D. Bougeard, K. S. Smirnov and E. Geidel, J. Phys. Chem. B 104, 9210 (2000).
- 2. M. Arab, D. Bougeard and K. S. Smirnov, Phys. Chem. Chem. Phys. 4, 1957 (2002).
- 3. M. Arab, D. Bougeard and K.S. Smirnov, Chem. Phys. Letters 379, 368 (2003).
- 4. W. W. Rudolph and C. C. Pye, Phys. Chem. Chem. Phys. 1, 4583 (1999).
- 5. M. Arab, D. Bougeard and K. S. Smirnov, Phys. Chem. Chem. Phys. 5, 4699 (2003).
- 6. M. Arab, D. Bougeard and K. S. Smirnov, Phys. Chem. Chem. Phys. (Submitted).