

## **Molecular modeling of the structure and dynamics of the interlayer and surface species of mixed-metal layered hydroxides: Chloride and water in hydrocalumite (Friedel's salt)**

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### **ABSTRACT**

The dynamical behavior of Cl<sup>-</sup> and H<sub>2</sub>O molecules in the interlayer and on the (001) surface of the Ca-aluminate hydrate hydrocalumite (Friedel's salt) over a range of temperatures from -100 to 300 °C was studied using isothermal-isobaric molecular dynamics computer simulations. This phase is currently the best available model compound for other, typically more disordered, mixed-metal layered hydroxides. The computed crystallographic parameters and density are in good agreement with available X-ray diffraction data and the force field developed for these simulations preserves the structure and density to within less than 2% of their measured values. In contrast to the highly ordered arrangement of the interlayer water molecules interpreted from the X-ray data, the simulations reveal significant dynamic disorder in water orientations. At all simulated temperatures, the interlayer water molecules undergo rapid librations (hindered hopping rotations) around an axis essentially perpendicular to the layers. This results in breaking and reformation of hydrogen bonds with the neighboring Cl<sup>-</sup> anions and in a time-averaged nearly uniaxial symmetry at Cl<sup>-</sup>, in good agreement with recent <sup>35</sup>Cl NMR measurements. Power spectra of translational, librational, and vibrational motions of interlayer and surface Cl<sup>-</sup> and H<sub>2</sub>O were calculated as Fourier transforms of the atomic velocity autocorrelation functions and compared with the corresponding spectra and dynamics for a bulk aqueous solution. The ordered interlayer space has significant effects on the motions. Strong electrostatic attraction between interlayer water molecules and Ca atoms in the principal layer makes the Ca...OH<sub>2</sub> bond direction the preferred axis for interlayer water librations. The calculated diffusion coefficient of Cl<sup>-</sup> as an outer-sphere surface complex is almost three times that of inner-sphere Cl<sup>-</sup>, but is still about an order of magnitude less than that of Cl<sup>-</sup> in bulk aqueous solution at the same temperature.