**FAR-INFRARED SPECTRA OF LAYERED DOUBLE HYDROXIDES: EXPERIMENTAL RESULTS AND MOLECULAR DYNAMICS SIMULATION FOR HYDROTALCITE.** R. James Kirkpatrick¹, Jianwei Wang¹, Andrey G. Kalinichev¹, X. Hou¹, and James E. Amonette². ¹Department of Geology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA. ²EMSL, Pacific Northwest National Laboratory, Richland, WA 99352 (kirkpat@uiuc.edu, jwang7@uiuc.edu, kalinich@uiuc.edu)

**Introduction:** Layered double hydroxides (LDHs), or hydrotalcite-like minerals (HTs), are an important class of natural and readily synthesized compounds with growing potential as anion-exchange and adsorption materials, carriers for drugs, antacids, electrode modifiers, catalysts, and catalyst supports [1-3]. Their layered crystal structures are similar to that of brucite, Mg(OH)₂, but develop permanent positive charge due to the isomorphic substitution of e.g., Al³⁺ for Mg²⁺. The positive charge is balanced by interlayer anions, which have associated water molecules. The combination of far-infrared spectroscopy and molecular mechanics simulations probes the low frequency atomic motions in these materials and provides significant insight into the structure and dynamics of the interlayer species in these phases. This paper presents results for a variety of Mgₓₓ₋ₓAlₓ LDHs.

**Far-infrared spectrum and MD simulations:**
Spectra were collected and molecular dynamics simulations were undertaken for three compositions:

- HT-Cl — [Mg₃Al(OH)₈]Cl·2H₂O;
- HT-CO₃ — [Mg₆Al₂(OH)₁₆]CO₃·3H₂O;
- HT-NO₃ — [Mg₃Al(OH)₆]NO₃·2H₂O.

Far-infrared spectra were collected in transmission mode using Bruker IFS66v/S and IFS 66/S spectrometers and standard FT-IR techniques. Excellent spectra could be obtained by grinding small amounts of powder onto one side of a piece of Scotch tape. Some samples were heated at either 225 or 275°C to remove interlayer water. These temperatures are below the dehydroxylation temperatures of these samples. MD simulations were performed to calculate power spectra of these compounds from velocity autocorrelations functions. The simulation supercell consisted of 6x6x1 (6x12x1 for HT-CO₃) crystallographic unit cells [2]. A modification of the consistent valence force field for ionic species was used for all ion-ion and ion-water interactions [4] and a flexible version of simple point charge potential was used for water. In addition to the interlayer anions and water molecules, all atoms of the hydroxide layer were also treated as completely movable. Isothermal-isobaric molecular dynamical simulations also allowed us to leave the size and shape of the simulation cell unconstrained [5,6]. The simulations were performed under ambient conditions (T=300 K, P=1 bar).

**Results and Discussion:** There is a major absorption band in all spectra near 350-480 cm⁻¹, which is independent of the interlayer anions and is associated with librational motions of OH-groups in the main hydroxide layer. The peak is smooth for HT-CO₃ but is split into several peaks for HT-NO₃ and HT-Cl. In the range of 50-300 cm⁻¹, the spectra are more anion-specific, showing different features for the three compounds. There are several clearly distinguishable absorption bands for HT-Cl, near 70-120, 150, 190, 220, and 250 cm⁻¹. The peaks are broader and less distinct for HT-CO₃ and HT-NO₃. The MD simulated power spectra reproduce well the main features of the experimental ones. Librational motions of the interlayer water molecules make different contributions to the spectra than those from the hydroxyl groups of HT main layers. Because of the higher negative charge on the carbonate ion, the frequency related to water librations is very close to that from OH groups, which makes the major peak smooth for HT-CO₃. Several spectral features in the range of 50-300 cm⁻¹ are related to the interactions among interlayer anions, water molecules, and hydroxyl groups of the main layers. For all three samples, the 70-120 cm⁻¹ band can be assigned to librational motions of the hydrogen-bonded network consisting of interlayer water molecules (and Cl⁻ in HT-Cl) in the xy crystallographic plane. The interlayer water also has a band near 220 cm⁻¹, which is associated with stretching vibrations of H-bonds in the z-direction (perpendicular to main layers). The 150 cm⁻¹ band is assigned to Mg vibrations in Mg(OH)₆ octahedra along the z-direction. There is a significant cooperativity of these vibrations, e.g., when one Mg atom is moving up, its Mg neighbors are moving down, and the main layer stays almost planar. Similarly, Al vibrations in the z-direction in Al(OH)₆ are centered near 190 cm⁻¹. The 250 cm⁻¹ band can be assigned to octahedral layer distortions, with both Mg and Al vibrating in the xy-plane.