

## **$^{15}\text{N}$ NMR study of nitrate ion structure and dynamics in hydrotalcite-like compounds**

**XIAOQIANG HOU,<sup>1,\*</sup> R. JAMES KIRKPATRICK,<sup>1</sup> PING YU,<sup>2</sup> DUANE MOORE,<sup>3</sup> AND YEONGKYO KIM<sup>1,†</sup>**

<sup>1</sup>Department of Geology, University of Illinois at Urbana-Champaign, 1301 W. Green Street, Urbana, Illinois 61801, U.S.A.

<sup>2</sup>Department of Material Science and Engineering, University of Illinois at Urbana-Champaign, 1304 W. Green Street, Urbana, Illinois 61801, U.S.A.

<sup>3</sup>Illinois State Geological Survey, 615 E. Peabody Drive, Champaign, Illinois 61820, U.S.A.

### **ABSTRACT**

We report here the first nuclear magnetic resonance (NMR) spectroscopic study of the dynamical and structural behavior of nitrate on the surface and in the interlayer of hydrotalcite-like compounds ( $^{15}\text{NO}_3\text{-HT}$ ). Spectroscopically resolvable surface-absorbed and interlayer  $\text{NO}_3$  have dramatically different dynamical characteristics. The interlayer nitrate shows a well defined, temperature independent uniaxial chemical shift anisotropy (CSA) powder pattern. It is rigidly held or perhaps undergoes rotation about its threefold axis at all temperatures between  $-100\text{ }^\circ\text{C}$  and  $+80\text{ }^\circ\text{C}$  and relative humidities (R.H.) from 0 to 100% at room temperature. For surface nitrate, however, the dynamical behavior depends substantially on temperature and relative humidity. Analysis of the temperature and R.H. dependences of the peak width yields reorientational frequencies which increase from essentially 0 at  $-100\text{ }^\circ\text{C}$  to  $2.6 \times 10^5\text{ Hz}$  at  $60\text{ }^\circ\text{C}$  and an activation energy of  $12.6\text{ kJ/mol}$ . For example, for samples at R.H. = 33%, the surface nitrate is isotropically mobile at frequencies greater than  $10^5\text{ Hz}$  at room temperature, but it becomes rigid or only rotates on its threefold axis at  $-100\text{ }^\circ\text{C}$ . For dry samples and samples heated at  $200\text{ }^\circ\text{C}$  (R.H. near 0%), the surface nitrate is not isotropically averaged at room temperature. In contrast to our previous results for  $^{35}\text{Cl}^-$ -containing hydrotalcite ( $^{35}\text{Cl}^-$ -HT), no NMR detectable structural phase transition is observed for  $^{15}\text{NO}_3\text{-HT}$ . The mobility of interlayer nitrate in HT is intermediate between that of carbonate and chloride.