

Anharmonic OH vibrations in brucite: Small pressure-induced redshift in the range 0–22 GPa

PAVLIN D. MITEV, GRZEGORZ GAJEWSKI, AND KERSTI HERMANSSON*

Materials Chemistry, The Angstrom Laboratory, Uppsala University, Box 538, S-75121 Uppsala, Sweden

ABSTRACT

The uncoupled anharmonic OH-stretching vibrational frequency for the layered mineral $\text{Mg}(\text{OH})_2$ (brucite) has been calculated in the pressure range 0–22 GPa. Quantum-mechanical electronic structure (DFT) calculations were performed, followed by quantum-mechanical vibrational energy calculations. The following findings emerged: (1) The calculated $\text{d}\nu(\text{OH})/\text{d}P$ slope is $-4 \text{ cm}^{-1}/\text{GPa}$, in agreement with the experimental literature value [taken as the average between the Raman and IR-measured slopes for $\text{Mg}(\text{OH})_2$]. (2) The calculated $\nu(\text{OH})$ vs. $R(\text{O}\cdots\text{O})$ correlation is linear and the slope is much smaller than that of traditional H-bond correlation curves in the literature. (3) The main origin of the small $\text{d}\nu/\text{d}P$ and $\text{d}\nu/\text{d}R(\text{O}\cdots\text{O})$ slopes is the small electric field variation as the mineral layers are pressed toward each other. (4) At high pressure, the OH^- ions show some tendency to be tilted with respect to the c axis, and a larger tilt angle leads to a larger $\nu(\text{OH})$ downshift. (5) The pressure variation of the D quadrupole coupling constant is approximately -1 kHz/GPa .

Keywords: Brucite, anharmonic OH frequencies, high pressure, electric field, hydrogen bonding, correlation curve, hydrous mineral