Vibrational spectroscopy of brucite: A molecular simulation investigation

PAUL S. BRATERMAN1,* AND RANDALL T. CYGAN2

1Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, Texas 76203, U.S.A.
2Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185-0754, U.S.A.

ABSTRACT

We have modeled the vibrational spectrum of brucite, the common phase of magnesium hydroxide, at 1 bar (10^5 Pa) by two separate techniques: molecular dynamics simulation and vibrational mode analysis. Molecular dynamics simulation of a model supercell provides information (from the power spectrum of the atomic velocity autocorrelation function) about the frequencies and directions of atomic thermal motions, using a defined energy force field. Vibrational mode analysis gives complementary information about the frequencies, nature, and infrared and Raman activity of the computed modes of the same system. Using both methods we find (in addition to the spectroscopically active modes) inactive modes up to around 1000 cm−1, corresponding to MOH bending (OH rotational) motions. We invoke these modes to explain the published inelastic neutron scattering data, and suggest that their relatively high frequency is an inevitable consequence of repulsive interactions between neighboring H atoms.

Keywords: Brucite, magnesium hydroxide, infrared, molecular dynamics, neutron scattering, vibrational spectra

INTRODUCTION

In this paper, we use two computational methods (molecular dynamics simulation and vibrational mode analysis) to examine the vibrational motions of brucite, Mg(OH)₂, at 1 bar, compare the results with those of traditional factor group analysis, and apply our findings to the interpretation of the experimental data for brucite, and, in particular, to the differences between the results of spectroscopy and those of inelastic neutron scattering. The results supplement those of the usual factor group analysis. Such an analysis gives the modes of the unit cell, which include all the infrared- and Raman-active modes of the solid, but these correspond only to the k = 0 vibrations, and turn out to be rather atypical.

Molecular simulations have been extensively applied to mineral systems in general (Cygan 2001), and to metal hydroxides and layered double hydroxides (LDH), in particular (Newman et al. 2001; Wang et al. 2003). Recently, we became interested in applying the technique to understand the effect of M²⁺:M³⁺ ratio in LDH, and conducted investigations of brucite as a way of validating the methodology. At this stage, we were surprised to discover that there are still outstanding issues regarding the brucite vibrational spectrum, and we are therefore reporting the results of our simulations, in the hope of shedding light on these, and, more generally, on the relationship between the results of different methods of investigation of mineral vibrations.

The vibrational behavior of brucite was discussed in detail, from both a group theoretical and an experimental perspective, in Mitra’s (1962) classic review, and has been the subject of numerous investigations since (e.g., Buchanan et al. 1963; Safford et al. 1963; Dawson et al. 1973; Kruger et al. 1989; Lutz et al. 1994; Weckler and Lutz 1996; Chakoumakos et al. 1997; Frost and Kloprogge 1999; de Oliveira 2001; Pracht et al. 2003; Ugliengo et al. 2004). Ryskin (1974) reviews the earlier work, and compares brucite with other hydroxides and oxyhydroxides. The relevant issues include the role of combination bands in adding complexity to the spectrum, the need to allow for the effects of contamination, especially in mineral specimens, and the nature of the hydrogen motions responsible for neutron scattering, which does not obey a symmetry-based selection rule. Further interesting questions arise regarding the effects of pressure, but we do not consider those here. Nor are we able to consider the combination bands found by many authors in the OH stretching region, since our methodology gives fundamentals only.

In molecular dynamics simulations of solids, periodic boundary conditions are imposed on a block of atoms, which for relatively simple materials, such as brucite, are chosen to be a supercell several times larger than the crystallographic unit cell. Within this simulation cell, the individual atoms are treated as classical particles, moving under the influence of a combination of covalent, electrostatic, and van der Waals forces. In the particular energy force field that we use, there is no explicit inclusion of hydrogen bonding (the possible role of which in brucite remains a matter for discussion; e.g., Kruger et al. 1989), since it is fully described by electrostatic interactions and dispersion forces. This is in accord with current views (Desiraju 2002), which assign an additional role to covalent interactions and dispersion forces. This is the absence of angular constraints on the metal hydroxide bond, other than those imposed by Coulomb forces, despite the partially covalent nature of the Mg-O bonds in brucite.

As pointed out by Cygan (2001) and Kubicki (2001), and the earlier work cited there, the Fourier transform of the atomic velocity autocorrelation function provides information about the