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Vibrational dynamics in H^+-substituted forsterite: A first-principles molecular dynamics study

Dawn M. Shaw and John S. Tse*

Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 5E2 Canada

Abstract

The vibrational spectra of H-substituted forsterite ($MgSiO_4H_2$) in which the Mg^{2+} at the M1 or M2 site is replaced by two H ions have been investigated by first-principles molecular dynamics calculations. Infrared spectra have been obtained and assigned with the aid of atomic vibrational density of states and the analysis of the atom radial distribution functions. It is shown that the proton dynamics are different at the M1 and M2 site. In the latter case, the proton does not remain bound to a single O atom but hops between O atoms in close proximity. This fluxional motion is highly temperature dependent. These fluxional motions results in substantially lower energy O-H stretching vibrations spanning a broad frequency range from 2000 to 3000 cm^{-1}. The present results will be useful for the characterization of the IR spectrum of H^+-substituted (leached) olivine under ambient conditions.

Keywords: Lattice dynamics, first-principles molecular dynamics, CPMD, olivine, forsterite, infrared spectroscopy