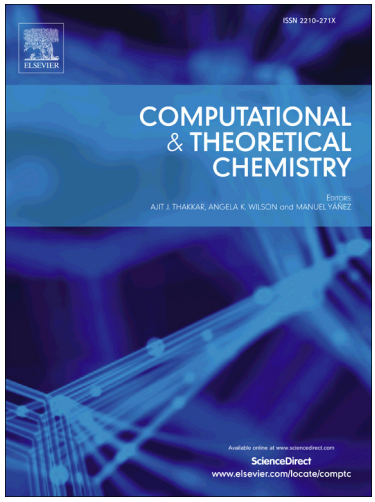

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Ab initio molecular dynamics simulation of infrared absorption spectra of crystalline sulfuric acid mono- and tetra-hydrates

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Abstract

Infrared absorption spectra of hydrated protons are very sensitive to the number and arrangements of water molecules. OH stretching absorption bands of Eigen cation ($H_9O_4^+$) are largely red-shifted to below 3000 cm^{-1}. Such largely red-shifted OH stretching bands are also observed in IR spectra of hydrochloric acid and sulfuric acid monohydrates in solid phase and hydrogen bonds of hydronium ion (H_3O^+) between three different ligand molecules are supposed to induce large red shift. However, while the narrow OH stretching bands of hydrochloric acid monohydrate has been successfully reproduced by ab initio molecular dynamics simulation, origin of the much broader OH stretching bands of sulfuric acid monohydrate has not been fully investigated. In this study we perform ab initio molecular dynamics simulation of sulfuric acid monohydrate whose crystal structure has been determined by X-ray diffraction. Dipole moments of ions in a unit cell are calculated their autocorrelation function is Fourier-transformed to obtain an IR spectrum which reproduces the largely red-shifted and broad OH stretching bands. The same procedure is also successfully applied to sulfuric acid tetrahydrate which contains Zundel type cation ($H_5O_2^+$) indicating capability of the method to simulate vibrational spectra of hydrogen bonded systems in condensed phase.

Keywords: Infrared spectra; sulfuric acid; hydronium ion; Zundel cation; hydrogen bond