Theoretical and Experimental Study of the Vibrational Spectra of Sarkinite $[Mn^{2+}_2(AsO_4)(OH)]$ and Adamite $[Zn_2(AsO_4)OH]$

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The arsenate hydroxyl-bearing minerals sarkinite and adamite were studied in terms of vibrational spectroscopy (IR and Raman) and quantum theoretical methods. The observed IR bands in the higher (1100–600 cm^{-1}) and especially lower (600–450 cm^{-1}) frequency region of AsO_4^{3-} vibrations could clearly discriminate between the studied analogues. The differences between their crystal structures are much pronounced in both IR and Raman OH-stretching regions. Namely, sole strong band is evidenced for orthorhombic adamite compared to four significantly weaker bands observed in corresponding IR and Raman spectral regions of monoclinic sarkinite. Essentially, all bands in the experimental spectra, collected at both room and liquid nitrogen temperature, were tentatively assigned. To support the tentative assignment of bands in the vibrational spectra of the mentioned minerals, periodic DFT calculations were carried out. Geometry optimizations of the 3D periodic systems were carried out employing a quasi-Newton optimization scheme. The required energy gradients were computed by the BFGS algorithm. Actually, at each optimization step, one-dimensional minimization was carried out using a second-order polynomial, which was followed by *n*-dimensional search using the complete second-derivative matrix. Subsequently to geometry optimization, numerical harmonic vibrational analysis was carried out, computing the dynamical matrix by numerical evaluation of the first-derivative of the analytical atomic gradients. In most cases, the assignments were either supported or implied by the obtained theoretical data. It is worth mentioning that this is the first experimental and theoretical study of the vibrational spectra of the very-rare sarkinite mineral.