

Theoretical analysis toward better description of the frequency shifts of the OH stretch of hydrogen-bonded water

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Relating vibrational properties to intermolecular configurations between vibrating solute and solvent molecules is generally important for correct analysis and interpretation of infrared and Raman spectra of condensed-phase systems^[1]. In the present study, a theoretical analysis in this direction is performed through calculations on (water)₉₀ clusters for better description of the OH stretch of hydrogen-bonded water^[2,3]. It is shown that the electric field descriptor related to the vibrating OH bond primarily describes the frequency shift arising from hydrogen-bond formation, whereas the secondary descriptors related to the other OH bond in the same water molecule noticeably improve the performance of theoretical modeling^[3]. It is also found that the electric charge configuration is an important factor for good performance of the electric field descriptor, while the secondary descriptors contribute to better description of the stretching modes of dangling OH bonds. Explicit forms of those descriptors consist only of coordinate data and, hence, may be applicable to spectral simulations through combination with classical molecular dynamics.

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