Imidazole vibrational frequency computation, solvent shifts, and resonance Raman simulation

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The vibrational spectroscopy of imidazole has been studied extensively both experimentally and computationally. The imidazole ring system is the chromophore of histidine and thus has key biological significance. Accurate computation of vibrational frequencies is challenging and computations tend to overestimate bond energy and thus raise the computed frequency particularly in the case of *ab initio* computation with Hartree-Fock components. Overestimation of vibrational frequencies arises in part from incomplete treatment of electron correlation. Even with robust treatment of correlation, errors due to neglect of anharmonicity can be large. Computational vibrational frequencies are usually computed with a harmonic analysis leading to systematic deviations from experimental observations. Furthermore, solvent can lead to dramatic shifts in vibrational frequencies that can provide the signature of local solvation environment. We develop and present a range of computational methods which we show can accurately reproduce gas phase vibrational frequencies with less than 10 cm^{-1} RMS error without using scaling factors. We model solvated imidazole vibrational frequencies using a combination of explicit and implicit solvation and are able to simulate resulting resonance Raman spectra.