

Investigating the Proton Transfer Dynamics and Vibrational Spectrum of Hydrogen Oxalate using Driven Molecular Dynamics Simulations

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In this computational chemistry work, we describe *ab initio* calculations and assignment of infrared (IR) spectra of an intramolecular H-bonding system hydrogen oxalate, $\text{C}_2\text{O}_4\text{H}^-$. The mechanism and dynamics of proton transfer are of fundamental importance in chemistry and biology. In $\text{C}_2\text{O}_4\text{H}^-$, proton transfer occurs along the non-linear path. Previous experimental studies are signaling very strong coupling between OH stretch mode and low frequency motions. We calculated IR spectra at 300 K using the direct molecular dynamics (MD) method at the MP2/aug-cc-pVDZ level of theory and assigned the prominent spectral features using the driven MD (DMD) method. The DMD method uses a sinusoidal electric field as a driving force to assist analyzing the complex anharmonic features exhibited by hydrogen oxalate anion. The barrier height for the proton transfer is 2.93 kcal/mol at the MP2/aug-cc-pVDZ level of theory. The low energy barrier for the proton transfer and hydrogen bonding interactions complicates the IR spectrum proton stretching region for hydrogen oxalate. The O-H stretch and bending modes are expected to undergo an anharmonic shift. As a result, the proton transfer absorption bands broadened over 2800 - 3200 cm^{-1} range. Based on DMD simulations, we found that the in-plane O-H bending mode shifted to $\sim 1390 \text{ cm}^{-1}$, in excellent agreement with experimental values, while the harmonic frequency is 1441 cm^{-1} at the MP2/aug-cc-pVDZ level of theory. While the in-plane bending mode and O-H stretching mode are reported to dominate the proton transfer, our calculations indicate that the proton transfer can easily occur as a result of mode coupling. The analysis of DMD trajectories provides atomic level insights into the proton transfer motion.