Elucidation of the Combination Bands and Anharmonic Features in the Vibrational Spectra of $C_2O_4H^-$ and $C_2O_4D^-$ with Driven Classical Trajectories

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Hydrogen bonds are strong electrostatic interactions characterized by the anharmonic shift of vibrational modes of atoms involved with this intramolecular force. The low energy barrier of the H^+ transfer in hydrogen oxalate ($C_2O_4H^-$), predicted to be ~2.98 kcal/mol at the MP2/aVDZ level of theory, allows for rapid proton exchange in the system and confounds the experimental vibrational spectrum of the molecule with broad spectral features in the O-H stretching region. The molecule is planar and exhibits several torsional motions among some of its lower frequency fundamental vibrational transitions. Because H-bonding and torsional motions often complicate the IR spectrum of a given system, there is a clear and present challenge to characterizing $C_2O_4H^-$ with vibrational spectroscopy. In this study, $C_2O_4H^-$ is simulated in a strong electric field, and classical trajectories are calculated using the Newtonian Equations of Motion to derive an accurate vibrational spectrum. At the MP2/aug-cc-pVDZ level of theory, we calculate the O-H stretch to be at ~3000 cm^{-1}, in reasonably good agreement with experimental results. The H in/out of plane bending modes are calculated to be 1390 cm^{-1} and 950 cm^{-1}, respectively, undergoing small anharmonic shifts as shown in the experiment. Although the experimental study did not detect lower frequency modes, the torsional modes are predicted to couple below the range that the experiment covered. Quartic Forcefield (QFF) based Vibrational 2nd Order Perturbation Theory (VPT2) calculations seem to agree with preliminary DMD calculations, predicting overtones at ~580 cm^{-1} ($2\nu_{14}$), ~830 cm^{-1} ($2\nu_{13}$), and a combination band at ~1703 cm^{-1} ($\nu_7 + \nu_9$).

KEYWORDS Proton transfer, hydrogen-bonding interaction, driven molecular dynamics, normal mode analysis, combination bands, isotopic substitution, anharmonicity.