

Model Calculations of H/D Isotope Substitution in Hydrogen Oxalate Anion Using the Normal Mode Analysis

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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, $C_2O_4H^-$. The study of H/D isotope effects can provide useful information on a proton's location inside a non-linear pathway. In $C_2O_4H^-$, a normal mode analysis was performed at the MP2/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ levels of theory. Previous experimental studies suggest a frequency shift $\sim 1000\text{ cm}^{-1}$ for the OH stretch mode upon the H/D isotopic substitution. Isotope calculations resulted in a shift of 842 cm^{-1} at the B3LYP/aug-cc-pVDZ level of theory. The O-H stretch and bending modes are expected to undergo an anharmonic shift. As a result, the proton transfer absorption bands broadened over $2800 - 3200\text{ cm}^{-1}$ range. The harmonic frequency of the OH in-plane bending mode in the hydrogen oxalate is 1441 cm^{-1} at the MP2/aug-cc-pVDZ level of theory. We have located the transition state for the proton transfer between two oxygens in the hydrogen oxalate. The imaginary frequency for this vibration is $1055i\text{ cm}^{-1}$ at the B3LYP/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 due to mode coupling.

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