CHIRAL TAG ROTATIONAL SPECTROSCOPY FOR CHIRAL ANALYSIS OF CARBOXYLIC ACIDS

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Chiral analysis, the determination of the absolute configuration of a chiral molecule and its enantiomeric excess, is a challenging analytical chemistry problem. Rotational spectroscopy can perform chiral analysis through either three-wave mixing spectroscopy, as introduced into the field by Patterson, Doyle, and Schnell, or through the chiral tag method. In chiral tagging, a small, chiral molecule serves as the chiral resolving agent and is attached to the analyte through noncovalent interactions. This work considers suitable tags to perform chiral analysis on carboxylic acids. 2-phenylpropionic acid was used to illustrate the proof-of-principle for chiral analysis of carboxylic acids using propylene oxide and butynol as the chiral resolving agent. Propylene oxide is found to have a functional group specific binding motif. Candidate chiral tag complex structures were evaluated using DFT calculations (B3LYP GD3BJ def2TZVP). The presence of these complexes in the pulsed jet sample were verified by comparison between experimental and theoretical rotational constants. Chiral tag measurements with propylene oxide pose a challenge because there are geometries for homochiral and heterochiral complexes with nearly identical rotational constants and dipole moment components. The close similarity makes it difficult to determine the absolute configuration to high confidence. However, the tag complexes of similar geometry have different relative energies for homochiral and heterochiral interactions. The lower energy conformers were more likely to be observed, indicating efficient cooling in the jet pulse. In this case, it appears that energetic considerations can be used to establish the absolute configuration. Methodology and analysis, as well as C^{13} structure fits and EE determination, will be further discussed.