PRECISE SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURES OF SULFUR-CONTAINING HETEROCYCLES: THIOPHENE (C₄H₄S) AND THIAZOLE (C₃H₃NS)

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As has recently been demonstrated with pyrimidine, using multiple isotopic substitution combined with coupled-cluster calculations treating the vibration-rotation interaction and the electron mass, it is possible to determine highly precise semi-experimental equilibrium structures ($r_{eSE}$). The CCSD(T)/cc-pCV5Z equilibrium structure of pyrimidine agrees with the $r_{eSE}$ structure within the 2σ uncertainties for all parameters. With the intent of improving the structure determinations of thiophene (8 – 360 GHz) and thiazole (130 -360 GHz), spectra have been collected. For each molecule, the main isotopologue vibrational ground state spectrum has been fit to a sextic Hamiltonian with low error (σ < 35 kHz). All heavy atom isotopologues ($^{34}$S, $^{13}$C, $^{15}$N, $^{33}$S) were detectable at natural abundance and similarly fit to sextic Hamiltonians. To obtain many more isotopologues, several deuteration strategies were employed: 1) acid-catalyzed H/D exchange, 2) base-catalyzed H/D exchange, and 3) lithium-halogen exchange using brominated forms of these species with subsequent addition of D₂O. These samples have resulted in a total of over two dozen isotopologues for each of the sulfur-containing heterocycles, including multiple substitutions of each atom. The resulting $r_{eSE}$ structures will be discussed, including an exploration of the number of isotopologues to sufficiently determine all parameters, computational treatment of the rotational constants, and comparison to theoretical $r_e$ structures containing sulfur. With pyrimidine, these structure determinations set a new standard of accuracy and precision for semi-experimental equilibrium structures ($r_{eSE}$).