COMPARISON OF AN IMPROVED SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURE (r_e^{SE}) OF KETENE TO A HIGH-LEVEL THEORETICAL EQUILIBRIUM STRUCTURE

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The millimeter-wave spectrum of ketene has been collected and analyzed from 130 GHz to 750 GHz and provided highly precise spectroscopic constants from a sextic S-reduced Hamiltonian. The synthesis of deuteriated samples enabled the spectroscopic measurements of five previously unreported ketene isotopologues. Combined with previous work, this resulted in a new highly precise and accurate semi-experimental (r_e^{SE}) structure for ketene from 32 independent moments of inertia. This r_e^{SE} structure was determined with the experimental rotational constants from all available isotopologues, together with computed vibration-rotation interaction and electron-mass distribution corrections from coupled-cluster singles, doubles, and perturbative triple calculations [CCSD(T)/cc-pCVTZ]. The 2σ uncertainties of the parameters of the r_e^{SE} are $\leq$ 0.007 Å and 0.014° for the bond distances and independent angle, respectively. Only S-reduced spectroscopic constants were used in the structure determination, due to a breakdown in the A reduction of the Hamiltonian for the most prolate ketene species. All four structural parameters are in agreement with the "best theoretical estimate" (BTE) calculated from the CCSD(T)/cc-pCV6Z r_e structure with corrections for extrapolation to the complete basis set, the incomplete treatment of electron correlation, the diagonal Born-Oppenheimer breakdown, and relativistic effects. The discrepancies between the current r_e^{SE} and previously reported r_e^{SE} structures will be discussed.