BROADBAND MICROWAVE AND COMPUTATIONAL STUDY OF HEXAFLUORO-O-XYLENE: HIGHLY COUPLED CF3 ROTORS

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The rotational constants and quartic centrifugal distortion coefficients of hexafluoro-o-xylene and all singly 13C isotopologues were precisely determined from the 8 to 18GHz gas phase microwave spectrum. A preliminary r0 structure was determined, reproducing the experimental rotational constants with deviations of no more than 15kHz. Interestingly, rather than the C2v symmetry structure expected intuitively, as in o-xylene, calculations with a variety of methods (B3LYP, CAM-B3LYP, ωB97XD, MP2, and CCSD(T)) predict a C2 symmetry structure in which the two CF3 groups rotate in opposite directions by about 16 degrees. Analysis of the interactions between the two CF3 groups using an effective fragment potential (EFP) approach identified two major contributions to their interaction, due to exchange repulsion and electrostatic repulsion, with electrostatic repulsion responsible for the barrier at the C2v geometry.

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