AB INITIO AND RESONANCE RAMAN STUDIES OF HEXAFLUORO-1,3-BUTADIENE

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Fluorine substitution can have a major effect on the electronic spectra and sometimes on the ground electronic state conformations of organic compounds. In this work we investigate the effect of perfluorination on the resonance Raman spectra of the simple diene, hexafluoro-1,3-butadiene (HFBD) where the preferred ground state geometry is believed to be skew s-cis. Ab initio calculations at the 6-31+G* level (which includes diffuse functions (+) and polarization functions (*) on both C and F atoms) together with MP2, BLYP-DFT and hybrid BLYP-DFT/HF treatments of electron correlation were performed. The most stable conformer of HFBD is confirmed to be the skew-cis form (ϕ = 58°) with a fundamental vibrational C-C torsional mode at 44 cm^{-1}. Ab initio calculations of the gradient of the potential energy surface of the resonant excited singlet state provide a prediction of the relative resonance Raman intensities. A detailed comparison of theory with experiment is possible and excellent agreement is observed. Activity in the fundamental transition of the torsional mode confirms the low frequency of this mode and the non-planar nature of the ground state. The origin of the preference of this molecule for a skew s-cis (in distinction to to a skew-s-trans) geometry is still unclear despite the ability of ab initio to calculate this preference.