SPECTROSCOPIC AND COMPUTATIONAL STUDIES OF MATRIX ISOLATED ISO-$CXBr_3$ (X=F, Cl, Br)

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Iso-polyhalomethanes are important reactive intermediates in the condensed and gas-phase chemistry of halomethanes. Building upon our recent study of iso-bromoform, in this work the substituted iso-tribromomethanes (iso-$CXBr_3$; X = F, Cl, Br) were characterized by matrix isolation infrared and UV/Visible spectroscopy, supported by $ab\ initio$ calculations, to further probe the structure, spectroscopy, properties, and photochemistry of these important intermediates. Selected wavelength laser irradiation of $CXBr_3$ samples in an inert rare gas (typically Ar; mixing ratio 1:500) held at $\sim$5 K yielded iso-$CXBr_3$ (XBrC-Br-Br or Br_2C-Br-X). The observed infrared and UV/Visible absorptions are in excellent agreement with computational predictions, and the energies of various stationary points on the $CXBr_3$ Potential Energy Surfaces (PESs) were characterized computationally using DFT, MP2, and CCSD(T) methods in combination with triple and quadruple-zeta quality basis sets. These calculations show that the isomers are minima on the PESs that lie $\sim$200 kJ/mol above the global $CXBr_3$ minimum, yet are bound by some 60 kJ/mol in the gas-phase with respect to the $CXBr_2$ + Br asymptote. Laser irradiation of the isomers resulted in back photoisomerization to $CXBr_3$, and intrinsic reaction coordinate (IRC) calculations confirmed the existence of a first order saddle point connecting the two isomers. Calculations of important stationary points on the $CXBr_3$ PESs show that in the gas-phase the isomerization barrier lies energetically near the threshold for simple bond fission. The iso-$CXBr_3$ species are significantly stabilized in the condensed phase, due to the high degree of ion-pair character, as revealed by Natural Resonance Theory analysis.