SPECTROSCOPIC AND COMPUTATIONAL STUDIES OF MATRIX ISOLATED ISO-CXBr$_3$ (X=F, Cl, Br)

AIMABLE KALUME, LISA GEORGE AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233*; BRIAN J. ESSELMAN, ROBERT J. MCMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706*.

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 ∼5 K yielded iso-CXBr$_3$ (XBrC-Br-Br or Br$_2$C-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 ∼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.