Halogen atoms are important reactive radicals in the atmosphere, and the reactions of these radicals often proceed through formation of a pre-reactive complex. In this work, pulsed jet discharge matrix isolation spectroscopy and computational methods were used to characterize pre-reactive complexes of halogen atoms with simple halons. Our experiments combined matrix isolation techniques with a pulsed DC discharge nozzle, where a dilute CH$_2$XBr (X=H,Cl,Br):rare gas sample was gently discharged and the products deposited onto a KBr window. The Br–BrCH$_2$X (X=H,Cl,Br) complexes were characterized by infrared and electronic spectroscopy, supported by ab initio and Density Functional Theory (DFT) calculations, which shed light on the structure of, bonding in, and binding energy of the complexes.