Multiphoton Photodissociation of Several Halocarbons. BOB QUANDT, Department of Chemistry Illinois State University — The 2 x 193 nm photodissociations of CHCl₃, CFCl₃, CF₃CCl₃, CCl₄, CH₃CCl₃ and CH₃CH₂CCl₃ have been examined using dispersed fluorescence. It was found that the initial photodissociation of CHCl₃ forms large amounts of CH(A₂∆) while the photodissociation of CCl₄ forms lesser but still significant amounts of CX(A₂∆). The photodissociations of CH₃CCl₃ and CH₃CH₂CCl₃ produce CH₃-C and CH₃CH₂-C presumably in the A₂∆ state. The exact photoproducts of the fluorinated species are currently unknown. Fluorescence rise time measurements show that the CH(A₂∆) and CCl(A₂∆) photoproducts quickly react to form C₂(d³Πg). However, formation of C₂(d³Πg) is attenuated when the primary photoproducts are CF₃C, CH₃-C and CH₃CH₂-C and disappears completely when it is CF. In addition, the atomic and molecular halogen photoproduction channels were investigated using ab initio calculations. Intrinsic Reaction Coordinate calculations were performed at the MP2 level of theory using the LANL2DZ basis set in order to characterize the dissociation pathways for all of species investigation. The results of the calculations show the presence of three transition states and an ion-pair isomer intermediate for all molecules. The broken symmetry structure of the transition states for the formation of molecular bromine is in agreement with the first step of the addition mechanism proposed by Cain and co-workers for CX₂+Y₂ reactions.