

Abstract Submitted
for the MAR06 Meeting of
The American Physical Society

Multiphoton Photodissociation of Several Halocarbons. BOB QUANDT, Department of Chemistry Illinois State University — The 2 x 193 nm photodissociations of CHCl_3 , CFCl_3 , CF_3CCl_3 , CCl_4 , $\text{CH}_3\text{-CCl}_3$ and $\text{CH}_3\text{CH}_2\text{-CCl}_3$ have been examined using dispersed fluorescence. It was found that the initial photodissociation of CHCl_3 forms large amounts of $\text{CH}(\text{A}^2\Delta)$ while the photodissociation of CCl_4 forms lesser but still significant amounts of $\text{CX}(\text{A}^2\Delta)$. The photodissociations of $\text{CH}_3\text{-CCl}_3$ and $\text{CH}_3\text{CH}_2\text{-CCl}_3$ produce $\text{CH}_3\text{-C}$ and $\text{CH}_3\text{CH}_2\text{-C}$ presumably in the $\text{A}^2\Delta$ state. The exact photoproducts of the fluorinated species are currently unknown. Fluorescence rise time measurements show that the $\text{CH}(\text{A}^2\Delta)$ and $\text{CCl}(\text{A}^2\Delta)$ photoproducts quickly react to form $\text{C}_2(\text{d}^3\Pi_g)$. However, formation of $\text{C}_2(\text{d}^3\Pi_g)$ is attenuated when the primary photoproducts are CF_3C , $\text{CH}_3\text{-C}$ and $\text{CH}_3\text{CH}_2\text{-C}$ and disappears completely when it is CF . In addition, the atomic and molecular halogen photoproduct 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 CX_2+Y_2 reactions.

Bob Quandt
Department of Chemistry Illinois State University

Date submitted: 11 Nov 2005

Electronic form version 1.4