STRUCTURE OF THE PHOTOCHEMICAL REACTION PATHWAYS POPULATED VIA THE PROMOTION of CF_2I_2 and CH_2I_2 INTO THEIR FIRST ELECTRONICALLY EXCITED STATES

P. Z. EL-KHOURY, A. N TARNOVSKY, and M. OLIVUCCI, *Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403*.

The photochemical reaction pathways following the promotion of CF_2I_2 and CH_2I_2 into their lowest lying electronically excited states are reported. The pathways are mapped using the complete active space self-consistent field (CASSCF) method. The S_0 to S_1 transitions in both molecules are found to be n to sigma* type transitions. The relaxation of the electronically excited CF_2I_2* and CH_2I_2* molecules from the initially excited Frank-Condon (FC) region to the product wells on the ground-state potential energy surface are found to occur via conical intersections. The results from our computational investigations explain the selectivity of photoproduct formation previously observed in gas-phase experiments on one hand, where some obvious conclusions about the condensed-phase photochemistry of these molecules can also be drawn.