MATRIX ISOLATION AND COMPUTATIONAL STUDY OF iso-CF_2Br_2: A ROUTE TO MOLECULAR PRODUCTS IN CF_2Br_2 PHOTOLYSIS

LISA GEORGE, AIMABLE KALUME AND SCOTT A. REID, *Department of Chemistry, Marquette University, Milwaukee, WI 53233*; PATRICK Z. EL-KHOURY AND ALEXANDER TARNOVSKY, *Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403*.

The photolysis products of dibromodifluoromethane following selected wavelength laser irradiation were characterized by matrix isolation infrared and UV/Visible spectroscopy, supported by ab initio calculations. Photolysis at wavelengths of 240 and 266 nm of CF_2Br_2:Ar samples (1:5000) held at 5 K yielded iso-CF_2Br_2 (F_2CBrBr), a weakly bound isomer of CF_2Br_2, which is characterized here for the first time. The observed infrared and UV/Visible absorptions of iso-CF_2Br_2 are in excellent agreement with computational predictions at the B3LYP/aug-cc-pVTZ level. Single point energy calculations at the CCSD(T)/aug-cc-pVDZ level on the B3LYP optimized geometries show that the iso-form is a minimum on the CF_2Br_2 potential energy surface, lying some 55 kcal/mol above the CF_2Br_2 ground state. The energies of various stationary points on the CF_2Br_2 PES were characterized computationally; taken with our experimental results, these show that iso-CF_2Br_2 is an intermediate in the Br + CF_2Br reaction leading to molecular products (CF_2 + Br_2). The photochemistry of the iso-form was also investigated; excitation into the intense 359 nm absorption band resulted in isomerization to CF_2Br_2. Our results are discussed in view of the rich literature on the gas-phase photochemistry of CF_2Br_2, particularly with respect to the existence of a roaming atom pathway leading to molecular products.