

MATRIX ISOLATION AND COMPUTATIONAL STUDY OF iso-CF₂Br₂: A ROUTE TO MOLECULAR PRODUCTS IN CF₂Br₂ PHOTOLYSIS

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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 CF₂Br₂:Ar samples (1:5000) held at 5 K yielded iso-CF₂Br₂ (F₂CBrBr), a weakly bound isomer of CF₂Br₂, which is characterized here for the first time. The observed infrared and UV/Visible absorptions of iso-CF₂Br₂ 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 CF₂Br₂ potential energy surface, lying some 55 kcal/mol above the CF₂Br₂ ground state. The energies of various stationary points on the CF₂Br₂ PES were characterized computationally; taken with our experimental results, these show that iso-CF₂Br₂ is an intermediate in the Br + CF₂Br reaction leading to molecular products (CF₂ + Br₂). The photochemistry of the iso-form was also investigated; excitation into the intense 359 nm absorption band resulted in isomerization to CF₂Br₂. Our results are discussed in view of the rich literature on the gas-phase photochemistry of CF₂Br₂, particularly with respect to the existence of a roaming atom pathway leading to molecular products.