

ROAMING ISOMERIZATION OF PHOTOEXCITED HALOGENATED ALKANES IN THE GAS AND LIQUID PHASES ^a

VENIAMIN A. BORIN, SERGEY M. MATVEEV, DARYA S. BUDKINA, CHRISTOPHER M. HICKS, ANDREY S. MERESHCHENKO, EVGENIIA V. BUTAEVA, VASILY V. VOROBYEV, ALEXANDER N TARNOVSKY, *Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH, USA.*

Recent experimental and computational gas-phase studies have brought to light a new type of unimolecular decomposition called a “roaming mechanism. It has only been observed in the gas phase, and whether it also occurs in solution is an intriguing question. Using ultrafast transient absorption spectroscopy, we report direct isomerization of CHBr_3 , BBr_3 , and PBr_3 geminal tribromides in solution within the first 100 fs after S_1 -excitation. The gas-phase conditions do not affect the earliest course of similar isomerization of CHBr_3 . High-level ab initio simulations on XBr_3 ($X = \text{B}, \text{P}, \text{and CH}$) suggest that isomerization is governed by an energetically and dynamically accessible S_1/S_0 conical intersection and can be best described as a roaming-mediated pathway. Following the initial relaxation from the Franck-Condon point, “wandering” of the central atoms and migration of Br atom starts on a planar region of the S_1 surface, and in the vicinity of the conical intersection (40 fs) the XBr_2 and Br fragments become separated to $\geq 3 \text{ \AA}$. After passage through the conical intersection, the partially dissociated bromine atom slips off the XBr_2 bisector plane, and forms the Br–Br bond of the BrXBr–Br isomer (60 fs). We give examples of similar roaming isomerization in several other di- and polyhalogenated alkanes.

^aThe authors gratefully acknowledges grants from the National Science Foundation (CHE-0847707, 0923360, and 1626420) which supported this work.