ISOMER-SPECIFIC SPECTROSCOPY OF GAS-PHASE α-HYDRONAPHTHYL, β-HYDRONAPHTHYL, AND 1,2,3-TRIHYDRONAPHTHYL RADICALS

JOSHUA A. SEBREE, TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907*; VADIM V. KISLOV, ALEXANDER M. MEBEL, *Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199*.

The jet-cooled two-color, resonant two-photon ionization (2C-R2PI) spectra for α-hydronaphthyl, β-hydronaphthyl, and 1,2,3-trihydronaphthyl radicals have been collected in the region from 18900-23400 cm^{-1}. Radicals were produced with an electric discharge of a select precursor in argon prior to supersonic expansion. 1,4-dihydronaphthalene and tetralin (1,2,3,4-tetrahydronaphthalene) were used to obtain spectra of the α-hydronaphthyl and 1,2,3-trihydronaphthyl radicals respectively. Discharge of 1,2-dihydronaphthalene yielded the α-hydronaphthyl radical spectrum with additional peaks that were tentatively assigned to the β-hydronaphthyl radical. Visible-visible holeburning was used to confirm this assignment. The S_0-S_n origins of the α-hydronaphthyl (18949 cm^{-1}), β-hydronaphthyl (19363 cm^{-1}), and 1,2,3-trihydronaphthyl radicals (21372 cm^{-1}) are in the visible region of the spectrum. Two-color photoionization efficiency scans were used to measure the adiabatic ionization potentials for the three free radicals to high accuracy. All three radicals have low ionization energies ($<$6.65 eV) compared to that of their precursors ($>$8 eV). A thermochemical cycle using these ionization potentials produces the C-H bond dissociation energy for the three free radicals, with values of 121.2, 103.6, and 168 kJ/mol for α-hydronaphthyl, β-hydronaphthyl, and 1,2,3-trihydronaphthyl radical respectively. It is proposed that these resonantly stabilized radicals may play an important role in photochemical processes in Titans atmosphere and the interstellar medium because of the extra stability gained from delocalizing the radical across the neighboring conjugated π system.