

MIND THE SINGLET-TRIPLET GAP: PHOTOELECTRON SPECTROSCOPY OF 1,3,4,6,9B-PENTAAZAPHENALENE

KENNETH WILSON, ETIENNE GARAND, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA.*

The vast majority of closed-shell organic molecules follow Hund's rule, namely: their first excited triplet state ( $T_1$ ) lies energetically below their first excited singlet state ( $S_1$ ). Recent computational studies, however, suggest that energetic inversion of these states is possible in a family of closed-shell species known as azaphenalenenes. The phenomenon is believed to arise from (i) minimal overlap between highest-occupied and lowest-unoccupied molecular orbitals, and (ii) stabilization of the  $S_1$  state via coupling to higher-excited electronic configurations. Despite experimental efforts to confirm  $S_1$ - $T_1$  inversion in an azaphenalenene species using optical techniques (1), quantification of the  $T_1$  energy—and thus the  $S_1$ - $T_1$  gap—is precluded by the spin selection rule. Using photoelectron spectroscopy, which circumvents the spin selection rule, we report a  $S_1$ - $T_1$  gap for 1,3,4,6,9b-pentaazaphenalenene of either  $374\text{ cm}^{-1}$  or  $-374\text{ cm}^{-1}$  ( $\pm 46\text{ meV}$ ), pending definitive assignment of the  $S_1$  state. Once confirmed, these results will have important implications in the fields of organic light-emitting diodes, catalysis, and benchmarking for high-level quantum chemical calculations of electronically excited states. (1) Ehrmaier et al. *J. Phys. Chem. A* 2019, 123 (38), 8099–8108.