DRIVING ADIABATIC AND NONADIABATIC PHOTODISSOCIATION OF PHENOL

MICHAEL L. HAUSE, Y. HEIDI YOON, AMANDA S. CASE, F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.*

The UV photochemistry of phenol involves the three lowest electronic states S_0, $S_1(^1\pi\pi^*)$, and $S_2(^1\pi\sigma^*)$. The UV absorption spectrum of phenol is dominated by the S_1-$S_0(\pi^* \leftarrow \pi)$ transition. Accessing the $S_1(^1\pi\pi^*)$ alone does not result in phenol dissociation. Rather, coupling the first excited state with the dissociative $S_2(^1\pi\sigma^*)$ state allows formation of phenoxyl and hydrogen atom products. Theoretical studies conducted by Lan, $et. al.$ [a] predict that the $S_2(^1\pi\sigma^*)$ state cuts through both the first excited and ground state of phenol. These two curve crossings become conical intersections along the O$-$H stretching coordinate in planar geometries. The S_0/S_2 conical intersection determines the branching between the ground and excited state phenoxyl products, where the ground electronic state correlates to excited state phenoxyl fragments and S_2 correlates to ground state phenoxyl fragments. Initial vibrational excitation can affect how molecules access or avoid conical intersections, as exhibited by our group's previous ammonia studies. Given the theoretical work by Lan $et.al.$, we expect initial O$-$H vibrational excitation to result in less ground state products. Using velocity map ion imaging, we measure kinetic energy distributions and angular distributions of these vibrationally mediated experiments. Dynamical effects of other vibrations of phenol will also be studied.

---

[a] Z. Lan, W. Domcke, V. Vallet, A. L. Sobolewski, and S. Mahapatra, *J. Chem. Phys.* **122**, 224315 (2005).