## THEORETICAL INVESTIGATION OF A NONADIABATIC MECHANISM FOR ALKYLPERNITRITE DECOMPO-SITION

JOHN M. HERBERT, Department of Chemistry, University of California, Berkeley, CA 94720; ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210; and JOHN F. STAN-TON, Department of Chemistry and Biochemistry, University of Texas, Austin, TX 78712.

We investigate a nonadiabatic two-state mechanism for reaction of alkylperoxyl radicals (ROO) with nitric oxide, an important step in the tropospheric ozone cycle. In our proposal, which is supported by high-level *ab initio* electronic structure calculations for  $R = CH_3$ , the pernitrite adduct ROONO propagates initially on a diabatic potential surface that correlates asymptotically with the  $\tilde{A}^2B_2$  state of NO<sub>2</sub>. This potential intersects a second diabatic potential corresponding to the stable nitrate species  $RNO_2$ , which correlates with ground-state  $(\tilde{X}^2A_1) NO_2$ . Near the intersection of these two surfaces, ROONO exhibits substantial diradical character. Diabatic potentials for the model system FONO have been developed based on CCSD(T)/cc-pVTZ electronic structure calculations. Here we report the results of classical and quantum dynamics simulations for FO + NO  $\rightarrow$  FONO  $\rightarrow$  FNO<sub>2</sub>.