STUDIES OF THE EXCITED STATE DYNAMICS OF HALOGEN OXIDES: INSIGHTS FROM STATE-TO-STATE PHOTODISSOCIATION EXPERIMENTS

SIMON W. NORTH, *Department of Chemistry, Texas A&M University, College Station, TX 77842St*.

The spectroscopy of the halogen oxides, in particular the characterization the bound X $^2\Pi_\Omega$ and A $^2\Pi_\Omega$ states, has been previously reported. Our focus has been on characterizing the low-lying dissociative states in these systems using velocity map ion imaging to analyze the the nascent photofragments. The talk will highlight our recent results on the predissociation dynamics of the ClO A $^2\Pi_{3/2}$ state through the measurements of final correlated state branching ratios, i.e. Cl($^2P_{J=3/2,1/2}$) + O($^3P_{J=2,1,0}$) channels, for single vibrational states. We find that the branching ratios are highly variable and depend strongly on v' providing a window into the v'-dependent predissociation mechanism. A comparison of the experimental results with the recent model of Lane et al. (Phys. Chem. Chem. Phys. 1, 3086 (1999)) in both the diabatic and adiabatic limits suggests that the dynamics are closer to the diabatic limit but suggest the need for more sophisticated quantum dynamical calculations to accurately describe the correlated fine structure branching ratios in this system. 'Continuum spectroscopy' above the A $^2\Pi_\Omega$ threshold has also been investigated for ClO and the results are in good agreement with recent ab inito calculations. Preliminary work on the excited state dynamics of BrO, both above and below the A $^2\Pi_\Omega$ threshold, will also be presented. These systems nicely illustrate the interplay between dynamical and spectroscopic studies.