MPIRD of SF_6^- and SF_5^- AND IMPLICATIONS FOR QET AUTODETACHMENT LIFETIMES

J.D. STEILL, R. N. COMPTON, *Department of Chemistry, The University of Tennessee, Knoxville, TN 37922*; J. R. EYLER, *Department of Chemistry, The University of Florida, Gainesville, FL 32611*; J. OOMENS, *FOM Institute for Plasma Physics 'Rijnhuizen', Nieuwegein, The Netherlands*.

Recent infrared multi-photon dissociation (IRMPD) experiments of SF_6^- and SF_5^- anions done with the FELIX free electron tunable infrared laser in the spectral range of 450-850 cm^{-1} are presented. Dissociation of $SF_6^- \rightarrow SF_5^-$ + F is observed in a strong broad resonance at 670 cm^{-1}, which is assigned to the anion ν_3 mode. The vibrational spectroscopy of negative molecular ions is crucial towards understanding the dynamics of electron transfer processes, as well as providing experimental validation for computational models of molecular bonding in anions. Many molecular negative ions have been shown to exhibit long (i.e. $> 1\mu s$) lifetimes with respect to electron autodetachment, and a recent reformulation of QET, or quasi-equilibrium theory, has shown success in reproducing these experimental lifetimes for a variety of molecules. In particular, the SF_6^- anion has an interesting history of disparate results for autodetachment lifetime measurements, largely dependent upon the type of experimental method employed. Analysis of the experimental data in reference to the theoretical predictions of QET suggests this disparity may be related to the degree of IVR, or inter-vibrational coupling occurring in the anion. Calculation of the electron autodetachment lifetime according to QET requires accurate values for the electron affinity as well as the vibrational frequencies for both the neutral and the anion. Ab-initio and DFT computations are extremely useful for providing reasonable estimates of the anion vibrational frequencies, however, experimental constraints upon these values are essential. In this context, IRMPD and recent attempts to acquire FT-IR emission spectra of these species is discussed. An additional benefit of anion vibrational spectroscopy is the elucidation of molecular structure and symmetry, in this case the expected O_h symmetry of the SF_6^- anion is confirmed, and this result combined with ab-initio potential energy surface calculations can provide a basis for interpretation of SF_6^- photoelectron spectra.