Photodetachment photoelectron spectroscopy (PES) is a powerful technique to investigate the electronic structure and chemical bonding of anions and the corresponding neutrals upon electron detachment. The Wang lab first introduced electrospray ionization (ESI) to spectroscopy by developing a magnetic-bottle PES apparatus with an ESI ion source to study multiply-charged anions. The development of the third-generation ESI-PES apparatus at Brown by coupling a cryogenically-controlled Paul trap with high-resolution PE imaging has enabled accurate vibrational and electronic information to be obtained for singly charged anions produced by ESI and the neutral radicals. In this talk, I will present my Ph.D. thesis research focusing on both non-resonant and resonant PES of cryogenically-cooled anions.

PES is usually done non-resonantly at fixed laser wavelength. I will discuss my first research project to accurately measure the electron affinity of an important organic molecule, tetracyanoquinodimethane (TCNQ). I will then present high-resolution studies on two fullerene anions encapsulating a water molecule: H2O@C60− and H2O@C59N−.

Anions with dipolar neutral cores can have dipole-bound excited states just below the electron detachment threshold. Optical excitations to vibrational levels of the dipole-bound state will induce vibrational autodetachment. The Wang lab has developed resonant PES via the dipole-bound excited states of anions. In the second part, I will talk about the observation of dipole-bound excited states in cryogenically-cooled phenoxide anions (C₆H₅O⁻).

Vibrational autodetachments from the dipole-bound states in the resonant PES result in highly non-Franck-Condon photoelectron spectra, which have shown to be an effective method to obtain vibrational information of dipolar neutral radicals. Finally, I will also present the first observation of an excited quadrupole-bound state in the 4-cyanophenoxide anion (NC(C₆H₅)O−), which shows similar autodetachment properties as the dipole-bound states.