

# *Ph.D. Dissertation Defense*

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Under the supervision of Professor Etienne Garand

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## Construction of an Anion Photoelectron Spectrometer for Investigating Singlet Fission in Molecular Clusters

The electronic structure of molecular systems is responsible for a wide range of phenomena including fluorescence, phosphorescence, lasers, and many effects in semi-conductors. One of the most remarkable is singlet fission, in which a singlet excitation on one molecule is split into two triplet excitations on neighboring molecules. These two triplets relax independently, and if integrated into a solar cell, singlet fission would raise the maximum theoretical efficiency of solar cells from 30% to 44%. Singlet fission is difficult to study due to its dependence on the interplay of singlet and triplet states, between which transitions are strongly forbidden. This work details the construction of an instrument capable of performing anion photoelectron spectroscopy, one of the few techniques with access to singlet and triplet states on equal footing. The spectrometer is a new design, capable of providing constant resolution over its entire range, and was used to observe the ground and first excited states of the polyaromatic hydrocarbons anthracene and fluoranthene, along with the simple aromatic oxide radicals phenoxy, 1-naphthoxy, and 2-naphthoxy. The spectra provide highly precise values for these species electron affinities and excited state term energies, along with vibrational frequencies for the Franck-Condon active modes.

The corresponding anions were produced via two different ion sources, both designed for the formation of molecular clusters. The anthracene and fluoranthene anions were produced via electron impact coupled to a supersonic expansion, the traditional method of cluster formation, while the aromatic oxides were produced via electrospray ionization. The electrospray source is coupled to a cryogenic linear octupole ion trap and equipped with a solid sample introduction system, allowing the formation of large anionic clusters containing phenols and carboxylic acids.

