Construction of the Cryo-cooled Ion Photodissociation Spectrometer:

During the time period of this grant, funds have been used to complete the construction of the cryo-cooled ion photodissociation spectrometer. At this point, the electron impact ion source has been developed and tested. It has been combined with the first quadrupole mass filter to allow a beam of mass-selected ions to be generated and detected using our Daly detector. The ion beam has been successfully turned using the quadrupole bender, and the cryo-cooled 22-pole ion trap has been designed and built. Electronics for the 22-pole ion trap are under construction, and the subsequent quadrupole bender and fragment mass selective quadrupole are ready to be mounted in the instrument. As soon as the electronics for the 22-pole trap are complete, we will begin working to trap ions. When this is successful, we will be ready to add the second quadrupole bender, fragment quadrupole mass filter, and Daly detector to complete the instrument. At that point we will begin searching for photodissociation spectra, first in molecules that are known to readily photodissociate, then in new molecules. One of our goals is to generate the gas-phase UO$_2^{2+}$ ion, and record its photodissociation action spectrum. This is a very challenging project, but is of high interest due to the current lack of understanding regarding the excited states of this important species.

Optical Spectra of UN:

In addition to the cryo-cooled ion photodissociation spectrometer, we have used these funds to collect spectra of diatomic UN, a molecule that is relevant to DOE interests in uranium nitride fuel. The experiment uses a pulsed laser to ablate a uranium sample into helium carrier gas that is seeded with a trace of NH$_3$. The UN molecules that are produced are then excited with a pulsed dye laser and the excited state of the molecule is then ionized by absorption of a 213 nm photon that is generated by the 5$^{th}$ harmonic of a Nd:YAG laser. As expected, the molecule has a complicated vibronic spectrum due to the large number of possible arrangements of electrons in the 5$f$, 6$d$, and 7$s$ orbitals. Preliminary rotationally resolved studies suggest that the ground state of the molecule has $\Omega=3.5$ with a bond length of approximately 1.76 Å, but further work is in progress to obtain a definitive result.
Thermochemistry and Reactivity of Th⁺:

The reactions of thorium cation with several atmospheric gases (N₂, O₂, CO₂, D₂O, CO) have been studied using guided ion beam tandem mass spectrometry. The reactions of Th⁺ with O₂ and CO₂ proceed exothermically to produce ThO⁺ with efficiencies comparable to the Langevin-Giomousis-Stevenson (LGS) collision cross sections of k/k_{LGS} = 1.21 ± 0.24 and k/k_{LGS} = 0.82 ± 0.16, respectively. These exothermic reactions indicate that D₀(Th⁺-O) > D₀(OC-O) = 5.55 eV. Additionally, ThO₂⁺ is formed endothermically in the reaction of Th⁺ with CO₂ with a reaction threshold of E₀ = 6.55 ± 0.12 eV, which suggests that D₀(Th⁺-2O) = 10.2 ± 0.2 eV. In the reaction of Th⁺ with D₂O, shown in Figure 3, formation of ThO⁺ (75%) and ThOD⁺ (25%) is observed with a total efficiency comparable to the average dipole orientation (ADO) model, k/k_{ADO} = 0.70 ± 0.14. ThD⁺ was also formed in this reaction with a threshold of E₀ = 4.80 ± 0.38 eV, which indicates that D₀(Th⁺-D) ≥ 0.40 ± 0.38 eV. In addition, the primary products were observed to undergo subsequent reactions to form both ThO₂⁺ and ThO₂D⁺. The reactions of Th⁺ with N₂ forms ThN⁺ in an endothermic process, with a measured threshold of E₀ = 3.07 ± 0.35 eV. This indicates that D₀(Th⁺-N) = 6.69 ± 0.35 eV. Cleavage of the very strong CO bond, D₀(C-O) = 11.1 eV, by Th⁺ is also observed to form ThO⁺ and ThC⁺, as shown in Figure 4. These data have been interpreted to yield threshold energies of 2.69 ± 0.28 and 7.58 ± 0.18 eV, respectively, which suggest that D₀(Th⁺-O) = 8.40 ± 0.28 eV and D₀(Th⁺-C) ≥ 3.50 ± 0.18 eV. The former value is consistent with the exothermic formation of ThO⁺ from O₂, CO₂, and D₂O, and when combined with D₀(Th⁺-2O) = 10.2 ± 0.2 eV, indicates that D₀(OTH⁺-O) = 1.8 ± 0.4 eV. In ongoing work, cross sectional data has been collected for the reactions of ThO⁺ with N₂, O₂, CO₂, and CO and the analysis of the data for thermodynamic information is proceeding.
Reactions with O₂, CO, and CO₂ all form ThO₂⁺ in endothermic processes, indicating that D₀(OTh⁺-O) < 5.1 eV. ThO⁺ also undergoes endothermic oxidations of CO to CO₂ and N₂ to N₂O to yield the Th⁺ atomic cation product. Reaction with N₂ also forms ThON⁺ in an endothermic process.

Figure 3. Cross sections for the reaction of Th⁺ with D₂O as a function of kinetic energy in the center-to-mass frame (lower) and lab frame (upper). The average dipole orientation (ADO) model cross section is shown as a solid line.

Figure 4. Cross sections for the reaction of Th⁺ with CO as a function of kinetic energy in the center-of-mass frame (lower) and lab frame (upper). The arrow indicates D₀(C-O) at 11.09 eV.

Unexpended Funds Remaining at the End of the Budget Period:

No unexpended funds remain from this grant.

Publications Resulting from this Grant:

No publications have yet resulted from this grant, although we will certainly be publishing at least one paper on the spectroscopy of UN, and several papers on the guided ion beam mass spectrometry studies of Th⁺.