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RPPR Final Report
as of 28-Jun-2022

Agency Code: 21XD

Proposal Number: 73852CHRIP

Agreement Number: W911NF-19-1-0182

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Final Report for Period Beginning 15-Mar-2019 and Ending 14-Sep-2020

Title: Acquisition of a laser desorption-time-of-flight mass spectrometry system for measuring ultrafast dissociation dynamics in energetic molecules

Begin Performance Period: 15-Mar-2019

End Performance Period: 14-Sep-2020

Report Term: 0-Other

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STEM Degrees: 1

STEM Participants: 6

Major Goals: The central objective of this proposal was the acquisition of new instrumentation to establish new research capabilities for investigating the decomposition dynamics of energetic molecules and materials. The instrumentation is intended to implement femtosecond laser desorption of energetic materials from solid thin films to produce gas-phase molecules and clusters, which will enable the investigation of decomposition dynamics on femtosecond through picosecond timescales. The specific tasks required to establish these capabilities are as follows:

1. Construct orthogonal acceleration-reflectron time-of-flight mass spectrometer (oa-RETOF MS) from purchased component parts and align the two laser beams into the chamber to produce ions from desorbed thin-film samples.
2. Detect ions in oa-RETOF MS instrument produced by (1) direct ionization of gas-phase molecules at the skimmer inlet source using strong-field ionization with femtosecond laser pulses from existing Ti:Sapphire laser and (2) direct ionization of desorbed analytes from thin-film samples.

Accomplishments: We successfully completed Goal (1) of instrument construction. Assembly of the instrument from the component parts was interrupted by COVID shut down of the lab between March and June 2020. Once the lab re-opened, instrument construction was completed. The vacuum system worked better than expected, giving a base pressure in the desorption chamber of 2 x 10-8 Torr when no sample was present. However, we found it necessary to incorporate an independent rough pump to pump down the desorption chamber from atmosphere after loading of a sample, which we obtained with no cost from extra pump supply in our department's instrumentation laboratory. In the current configuration, the desorption chamber can pump down to an adequate working pressure (below 10-7 Torr) after sample loading within a couple of hours. We also built a gas inlet to introduce volatile samples for testing and alignment of the ion detection instrumentation. When a gaseous or volatile liquid sample is introduced through this inlet, the pressure inside the desorption chamber can be up to 5 x 10-4 Torr while the pressure inside the flight tube remains at a pressure of 2 x 10-7 Torr, safe for the microchannel plate detector. Hence, in addition to serving as a useful feature for optimizing ion signals and laser beam alignment, this inlet can be used in the future to introduce a reactive gas that could react with desorbed samples, opening up further possible experiments on chemical reactivity. The additional goal of aligning both the desorption and postionization laser beams into the chamber was also completed. Photographs of the instrument with details of the the ion source and laser beam paths are provided in the uploaded document.

We were unable to complete Goal (2) of ion detection in the reporting period due to unexpected issues with the electronics and interfacing them with the existing electronics that control the postionization laser. We had to purchase an additional pulse generator to gate the voltage pulse imparted to the ion steering plate that directs the incoming ions orthogonally into the flight tube. This pulse generator was then interfaced with the signal delay generator (SDG) box that triggers the postionization laser such that the delay between the postionization laser pulse and the electrical voltage pulse for ion steering could be controlled. We also had to purchase an electrical preamplifier (ORTEC Model 9326) to increase detector sensitivity. Once these components were in place, optimization of ion detection could commence.

Training Opportunities: The following Ph.D. students worked on construction and testing of the instrument as part of their training:
Derrick Ampadu Boateng (Ph.D. 2020)
Shane McPherson (Ph.D. expected in 2023)
Hugo López Peña (Ph.D. expected in 2023)
Jacob Shusterman (Ph.D. expected in 2024)

The following undergraduate students contributed to testing of the instrument under supervision of Ph.D. student Shane McPherson:
Christine Dunstan (B.S. 2021)
Zachary Hughes (B.S. 2022)

Results Dissemination: Hosted groups of undergraduate students (both STEM and non-STEM majors) from VCU and University of Mary Washington for laboratory tours that demonstrated use of the lasers and mass spectrometers.

Honors and Awards: During reporting period, PI received the following awards:

1. PECASE in July 2019
2. VCU Outstanding Early Career Faculty Award in 2020

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)
Participant: Derrick Ampadu Boateng
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Shane McPherson
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Hugo López Peña
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Jacob Shusterman
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Christine Dunstan
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Zachary Hughes
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Partners

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I certify that the information in the report is complete and accurate:
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Signature Date: 6/16/22 5:27PM

Final Report on W911NF-19-1-0192

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This portion of the report describes features of the oa-RETOF MS instrument constructed with the grant. An overview of the instrument is shown in Figure 1. The desorption chamber contains quartz windows to admit the two laser sources: (1) the desorption laser (magenta arrow) and (2) the postionization laser (red arrow). The desorption laser is the Yb-doped fiber laser producing 300 fs, 1035 nm pulses at 500 kHz that was purchased with funds from this grant. The postionization laser is the pre-existing Ti:Sapphire laser that has been used in other experiments in grants W911NF-18-1-0051 and W911NF-19-1-0099. The flight tube portion of the RETOF containing the sensitive multichannel plate detectors can be isolated from the desorption chamber by a gate valve, which allows for opening the desorption chamber during laser alignment and sample manipulation without breaking vacuum in the flight tube. We have also installed a gas sample inlet (blue arrow) that allows for introduction of a gaseous or volatile liquid sample into the chamber. This is used for optimizing ion detection and fine-tuning the postionization laser alignment because it provides a high flux of molecules for ionization.

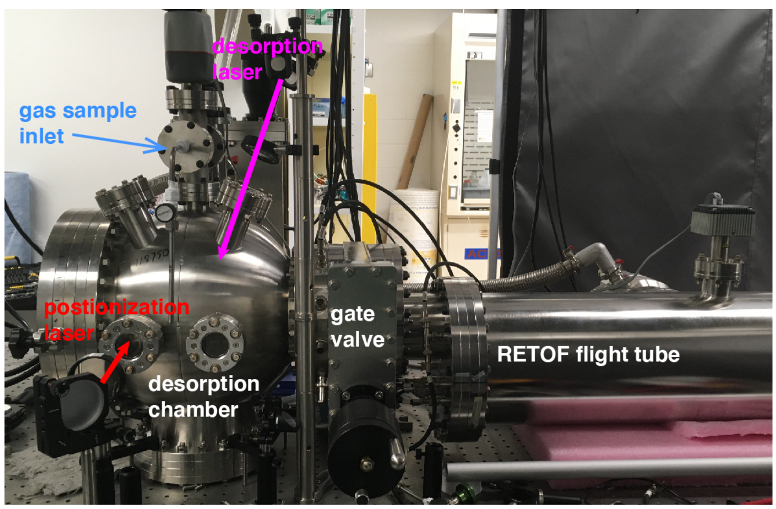

Figure 1: Photograph of oa-RETOF instrument with annotations.

Figure 2 shows details of the sample holder and ion source inside the desorption chamber. The desorption laser (magenta) is introduced from the top of the chamber and impacts the sample stage (which is shown with no sample attached). The sample stage is mounted on a 3D xyz motorized translation stage that makes it possible to move the sample during experiments so that a fresh sample is desorbed with each laser shot. Desorbed species intersect the path of the postionization laser, which is focused to a point directly in front of the skimmer to produce ions. During instrument testing, a gas sample is introduced into the area above the skimmer to produce a high density of species for ionization in front of the skimmer. The skimmer is polarized at -2500 V to admit cations, and the polarity can be reversed to admit anions. Ions admitted through the skimmer are accelerated orthogonally through the ion extraction source.

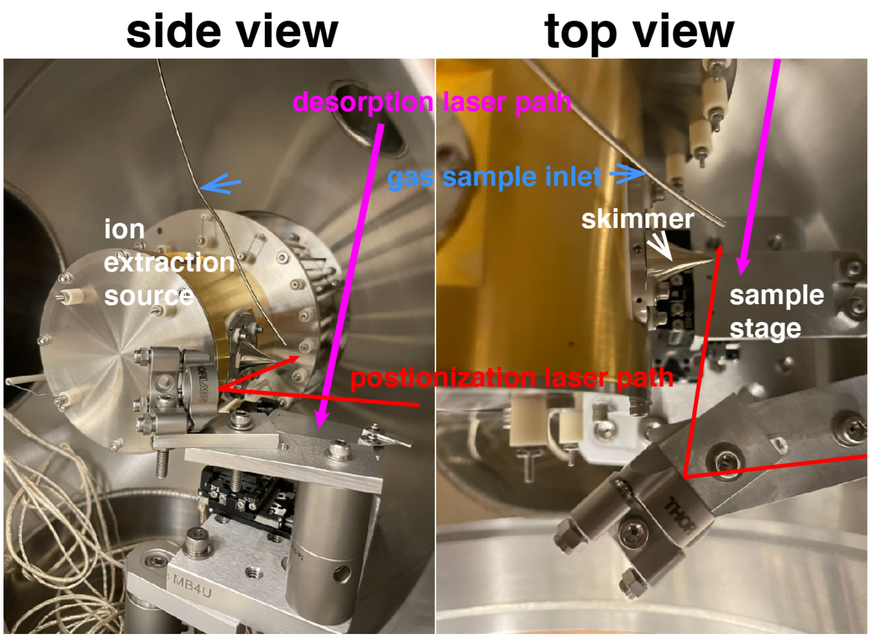

Figure 2: Photographs of interior of the desorption chamber from a side (left) and top (right) view. The beam paths of the desorption and postionization lasers, gas sample inlet, skimmer cone, and sample stage are shown.

To illustrate how ions are produced adjacent to the skimmer cone, Figure 3 shows a photograph taken with the postionization laser focused to produce a plasma when the desorption chamber is open to air. The blue light produced in the background comes from third-harmonic generation of the 1300 nm laser light induced by plasma formation.

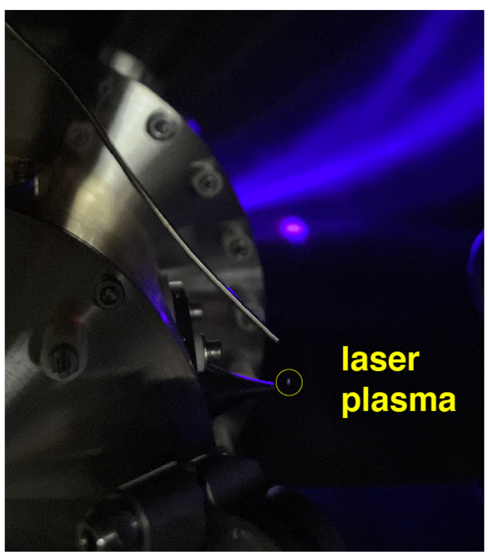

Figure 3: Photograph of postionization laser focused in front of the skimmer. The plasma is inside the yellow circle.