REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

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1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
15-11-2018	Final Report	15-Jul-2017 - 14-Jul-2018

4. TITLE AND SUBTITLE
Final Report: A Tunable Laser System for Interfacial Electron Transfer Measurements in Reactive Gas/Liquid Systems

5a. CONTRACT NUMBER
W911NF-17-1-0206

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611103

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Notre Dame
ND Research
940 Grace Hall
Notre Dame, IN 46556 -5708

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
70025-CH-RIP.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			David Go
UU	UU	UU	UU		19b. TELEPHONE NUMBER 574-631-8394

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

RPPR Final Report
as of 21-Nov-2018

Agency Code:

Proposal Number: 70025CHRIP **Agreement Number: W911NF-17-1-0206**

INVESTIGATOR(S):

Name: David M. Bartels
Email: dbartel1@nd.edu
Phone Number: 5746315561
Principal: N

Name: David Batten Go
Email: dgo@nd.edu
Phone Number: 5746318394
Principal: Y

Organization: **University of Notre Dame**
Address: ND Research, Notre Dame, IN 465565708
Country: USA

DUNS Number: 824910376 EIN: 350868188

Report Date: 14-Oct-2018 Date Received: 15-Nov-2018

Final Report for Period Beginning 15-Jul-2017 and Ending 14-Jul-2018

Title: A Tunable Laser System for Interfacial Electron Transfer Measurements in Reactive Gas/Liquid Systems

Begin Performance Period: 15-Jul-2017 **End Performance Period:** 14-Jul-2018

Report Term: 0-Other

Submitted By: David Go Email: dgo@nd.edu
Phone: (574) 631-8394

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: **STEM Participants:**

Major Goals: The goal of this DURIP was to purchase a laser system to study the electrochemistry at the interface of a reactive gas (plasma) and a liquid in order to support the efforts of ARO Grant W911NF-17-1-0119, whose goal is to establish a fundamental understanding of plasma-solvated electrons and the electrochemistry they promote. In short, when an atmospheric-pressure gas discharge is brought into contact with a liquid, both reducing and oxidizing species are injected into the liquid, promoting a wide variety of redox reactions. Our work particularly focuses on the nature and reaction pathways of plasma electrons injected into the liquid, plasma-injected solvated electrons.

In a prior ARO-sponsored STIR grant (W911NF-14-1-0241), we developed a new measurement technique called total internal reflection absorption spectroscopy (TIRAS, Supporting Figure 1) to measure the spectrum of the plasma-injected solvated electron (Supporting Figure 2) and using simple models, extract information such as reaction rate constants and the average penetration depth of the electrons into the solution. However, those spectral measurements and extracted quantities were limited by the use of discrete diode lasers in TIRAS and simplifying approximations in the models used for data analysis. Therefore, the aim of this DURIP was to purchase a continuous-wave, Ti:sapphire tunable laser to enable us to more completely measure and understand the spectrum.

Accomplishments: TIRAS Research Instrument: Through this DURIP, we purchased a Spectra-Physics Matisse 2 TR ring Ti:sapphire laser, the TIDYECW kit to convert the Matisse to a dye operation for the green wavelengths, and WaveTrain 2 frequency doubler to achieve blue and UV wavelengths. To pump the Matisse, a Coherent Verdi G20 OPSLaser-Diode System was also purchased. These instruments were installed on a newly-purchased Newport optical table in PI Go's laser lab (Supporting Figure 3). This DURIP also supported the purchased of the equipment to recreate the TIRAS measurement, allowing us to have redundant systems to support coordinated studies. This included a power supply to generate the plasma and a lock-in amplifier to operate in a pulsing mode. Finally, a new optical coupling system was installed, freely coupling the output of the Matisse into the TIRAS measurement, improving on the previous system by reducing the laser spot size to ~300 ⌒m at the plasma-liquid interface and reducing systematic uncertainty due to misalignment.

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as of 21-Nov-2018

Through our complementary ARO Grant W911NF-17-1-0119, we have begun conducting TIRAS measurements and benchmarking them against both the known spectrum of the solvated electron and our prior work. Supporting Figure 3 shows one such measurement, where we were more completely able to map out the peak of the spectrum. Note that it is apparently more consistent with the known solvated electron spectrum than our prior measurement using discrete diode lasers (Supporting Figure 2). While these results are extremely preliminary, one possible reason for this is that the improved optics of the new TIRAS system reduces the inherent systematic error in the system; meaning that the prior measurement with diode lasers was less accurate. Importantly, the new tunable laser has allowed a more refined measurement of the peak of the spectrum.

We are currently refining the system and our measurement technique in order to conduct a thorough comparative test to our prior work; if the spectrum does in fact change, we will certainly publish these updated results in a journal such as the Journal of Physical Chemistry Letters or Review of Scientific Instruments. After completing that study, we will explore how the spectrum behaves under different solvent conditions, and specifically high salt conditions that are known to alter the plasma itself (Rumbach et al., Phys Rev E, 95, 053203, 2017).

Auto-Fluorescence Research Instrument: Through good fortune, the original price for both the Matisse and Verdi lasers was significantly lower than the quotes provided when the proposal was written. This enabled us to utilize the remaining budget to develop an entirely new and novel experimental set-up to measure the fluorescence of plasma-injected electrons during the solvation phase.

The fully solvated electron typically exists in a localized ground state similar to an s-orbital. By absorbing a red photon, it becomes excited to a p-like orbital state. According to time-reversal symmetry, the excited state should be able to return to the ground state by emitting a red photon. That is, solvated electrons should exhibit a fluorescence spectrum that reflects their absorption spectrum and the relaxation dynamics of the excited state. However, a plasma-injected electron enters the liquid at a higher energy state, above that of the p-like orbital state. The question that has persisted is what is the energy path the electron follows before settling into the ground state. That is, does it first get trapped in a higher energy state and then quantum mechanically relax to the ground, emitting a photon in the process – what we call autofluorescence. Or does the electron simply dissipate its energy collisionally until finding a ground state, in which case there is no emission. Understanding and quantifying such behavior would not only be of great importance to the physical chemistry community, but allow us to better understand the solvation process and electron reactions that occur in the ‘pre-solvated’ state in plasma electrochemistry. Literature currently suggests that reaction rates for pre-solvated electrons are nearly 3 orders of magnitude greater than that of solvated electrons, creating the opportunity for an extremely reducing environment.

To attempt to measure and quantify auto-fluorescence, we have developed a spectroscopy system consisting of an inverted microscope and spectrometer, as sketched in Supporting Figure 4. The system is based on similar systems for conducting Raman spectroscopy in liquid systems, and thus we anticipate the system having much greater utility than only autofluorescence measurements, including a potential resonance Raman measurement that could utilize the above Matisse laser. We purchased a Nikon Ti2-U Inverted Manual Microscope and a Princeton Instruments FERGIE integrated spectrograph, as shown in Supporting Figure 4, along with supporting optics pieces. We have completed building the instrument and are beginning to characterize it.

Training Opportunities: Nothing to Report

RPPR Final Report
as of 21-Nov-2018

Results Dissemination: 1. Publications (during this reporting period)
(a) Papers published in peer-reviewed journals (0)
- None

(b) Papers published in non-peer-reviewed journals (0)
- None

(c) Presentations (8)
i. Presentations at meetings, but not published in Conference Proceedings
- H. E. Delgado*, D. C. Martin*, P. Rumbach, D. M. Bartels, D. B. Go, “Influence of plasma-generated species on the Faradaic efficiency of plasma-liquid systems,” IEEE International Conference on Plasma Science, Denver, CO, 2018. (presented by H. E. Delgado)
- P. Rumbach, H. E. Delgado*, D. M. Bartels, D. B. Go, “Theoretical Analysis of Free Radical Chemistry at a Plasma-Liquid Interface,” IEEE International Conference on Plasma Science, Denver, CO, 2018. (presented by P. Rumbach)
- D. C. Martin*, N. Turan*, P. Rumbach, D. B. Go , “Measuring the Radius of the Plasma at the Plasma-Liquid Interface in a Pulsed-Current, DC Discharge,” Annual Meeting of the Electrostatics Society of America, Boston, MA, 2018. (presented by D. Martin)
- H. E. Delgado*, P. Rumbach, D. M. Bartels, D. B. Go, “The Impact of Solution Chemistry on the Absorption Spectra of Plasma-Generated Solvated Electrons in Aqueous Solutions,” Gaseous Electronics Conference, Pittsburgh, PA, 2017. (poster by H. E. Delgado)
- P. Rumbach, J. P. Clarke, D. B. Go, “Electrostatic Debye Layer Formed at a Plasma-Liquid Interface,” Gaseous Electronics Conference, Pittsburgh, PA, 2017. (presented by D. B. Go)
- P. Rumbach, J. P. Clarke, D. B. Go, “The Electrostatic Debye Layer of the Plasma-Liquid Interface,” International Conference on Plasma Science, Atlantic City, NJ, 2017. (presented by P. Rumbach)

ii. Non-Peer-Reviewed Conference Proceeding publications (other than abstracts)
- None

iii. Peer-Reviewed Conference Proceeding publications (other than abstracts)
- None

(d) Manuscripts (0)
- None

(e) Books (1)
- D. B. Go, Ionization and Ion Transport: A primer for the study of non-equilibrium, low-temperature gas discharges and plasmas, Morgan & Claypool Publishers: San Rafael, CA, 2018. (ISBN 978-1-6817-4601-2) (published as part of the Institute of Physics (IOP) Concise Physics Series)

(g) Title of Patents Disclosed during reporting period (0)
- None

(h) Patents Awarded during the reporting period (0)
- None

Honors and Awards: Honor and Awards (3)
- D. C. Martin, Annual Meeting of the Electrostatics Society of America, Best Student Paper – 1st Place
- D. B. Go, Electrostatics Society of America Rising Star Award, 2018
- D. B. Go Institute of Electrical and Electronics Engineers (IEEE) Nuclear and Plasma Sciences Society (NPSS) Early Achievement Award, 2018

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Co PD/PI

RPPR Final Report
as of 21-Nov-2018

Participant: David M. Bartels
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Staff Scientist (doctoral level)
Participant: Paul Rumbach
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Hernan E. Delgado
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Daniel C. Martin
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Tunable Laser System for Interfacial Electron Transfer Measurements in Reactive Gas/Liquid Systems

W911NF-17-1-0206

Final Progress Report
July 15, 2017 – July 14, 2018

David B. Go (PI)
Department of Aerospace and Mechanical Engineering &
Department of Chemical and Biomolecular Engineering
University of Notre Dame, Notre Dame, IN 46556, USA

David M. Bartels (Co-PI)
Notre Dame Radiation Laboratory & Department of Chemistry and Biochemistry
University of Notre Dame, Notre Dame, IN 46556, USA

1. **Publications (during this reporting period)**

(a) Papers published in peer-reviewed journals **(0)**

- None

(b) Papers published in non-peer-reviewed journals **(0)**

- None

(c) Presentations **(8)**

i. Presentations at meetings, but not published in Conference Proceedings

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(g) Title of Patents Disclosed during reporting period **(0)**
- None

(h) Patents Awarded during the reporting period **(0)**
- None

2. Student/Personnel Metrics

(a) Undergraduate STEM Students: **0**

(b) Graduate STEM Students: **1**
- Hernan Delgado (% supported: 0%, %FTE: 0%) – supported by ARO Grant W911NF-17-1-0119
- Daniel Martin (% supported: 0%, %FTE: 0%) – supported by ARO Grant W911NF-17-1-0119

(c) STEM Students that Received Degree: **0**

3. Technology Transfer

There has been no intellectual property-based technology transfer to report (*e.g.*, no patents or start-up companies). Preliminary discussions of potential collaborations with the Naval Research Laboratory have taken place.

4. Scientific Progress and Accomplishments

***Background and Objectives*:** The **goal** of this DURIP was to purchase a laser system to study the electrochemistry at the interface of a reactive gas (plasma) and a liquid in order to support the efforts of ARO Grant W911NF-17-1-0119, whose goal is to establish a fundamental understanding of plasma-solvated electrons and the electrochemistry they promote. In short, when an atmospheric-pressure gas discharge is brought into contact with a liquid, both reducing and oxidizing species are injected into the liquid, promoting a wide variety of redox reactions. Our work particularly focuses on the nature and reaction pathways of plasma electrons injected into the liquid, plasma-injected solvated electrons.

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electron simply dissipate its energy collisionally until finding a ground state, in which case there is no emission. Understanding and quantifying such behavior would not only be of great importance to the physical chemistry community, but allow us to better understand the solvation process and electron reactions that occur in the 'pre-solvated' state in plasma electrochemistry. Literature currently suggests that reaction rates for pre-solvated electrons are nearly 3 orders of magnitude greater than that of solvated electrons, creating the opportunity for an extremely reducing environment.

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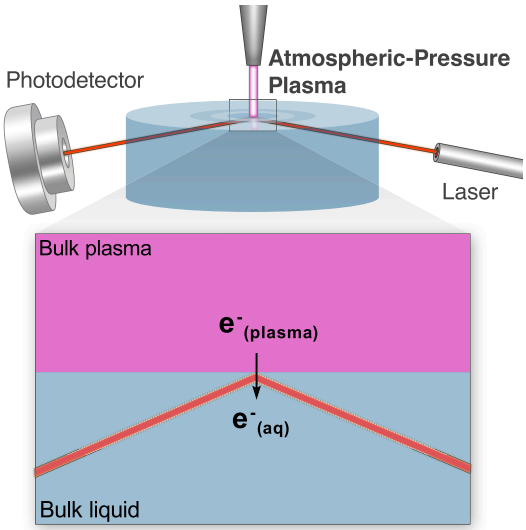
5. Copies of Technical Reports

None to report.

6. Supporting Figures

See following pages.



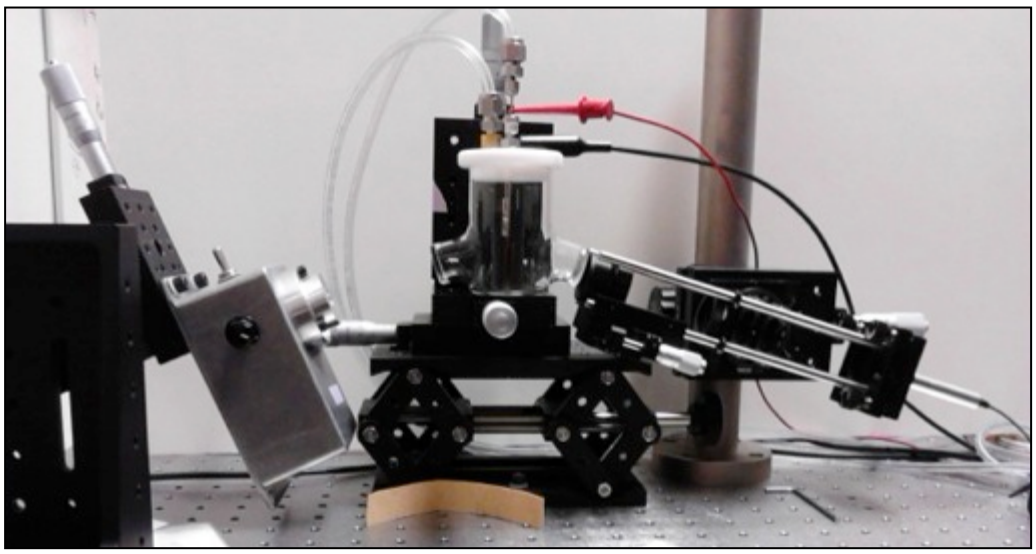


Figure 1. Generation and detection of solvated electrons by an atmospheric-pressure plasma (top) Schematic of optical absorption spectroscopy measurement to probe the interface of the plasma and liquid, where solvated electrons are detected by their optical absorption. A total internal reflection approach is used to increase the signal-to-noise and reduce the effects of spurious signals due to reflections off the interface. (bottom) Photograph of experimental set-up including the laser, plasma electrochemical cell, and photodetector.

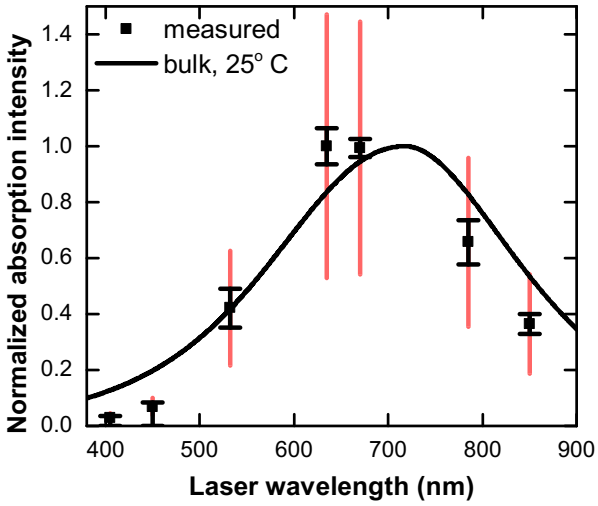


Figure 2. Measured absorption spectrum compared to bulk solvated electrons. Measured optical absorption signal corresponding to solvated electrons measured at the plasma-solution interface by using laser diodes at different wavelengths. Black error bars with capped ends represent the root mean square (RMS) variance in the raw data, and the overlaid red error bars also account for the systematic uncertainty in the laser-plasma overlap. Both sets of error bars represent 90% confidence. A Gaussian-Lorentzian bulk spectrum (solid line) measured in pulse radiolysis experiments for a temperature of 25°C [Bartels et al. *J. Phys. Chem. A* 109, 1299 (2005)] is included as a guide. The data indicate a blue shift to the left by approximately 50 nm as well as suppression of the Lorentzian tale at wavelengths less than 500 nm. These two features strongly suggest that the plasma-liquid environment is fundamentally different from other environments used to produce solvated electrons.

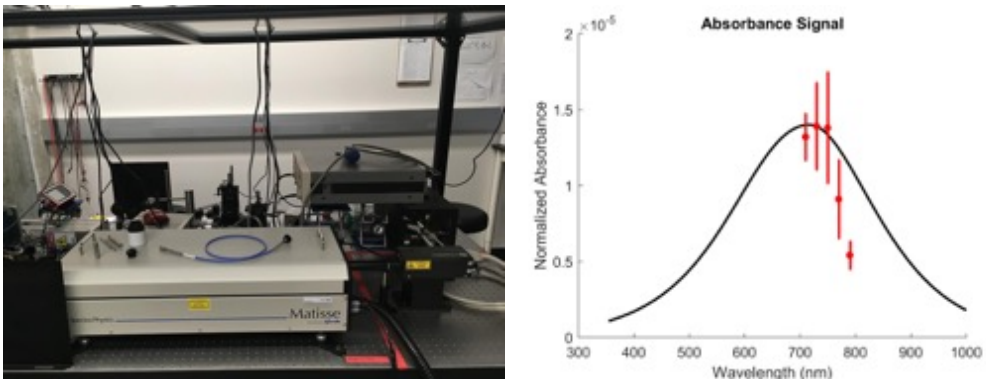


Figure 3. New TIRAS apparatus and initial measurements. (left) The new TIRAS system has a Ti:sapphire tunable laser that will enable more completing mapping out the spectrum from 700-800 nm, in order to reveal if the blue shift observed in Figure 2 is in fact real or an artifact of earlier versions of TIRAS. (right) An initial measurement of the absorption spectrum of plasma-injected solvated electrons. The system is currently undergoing more refinement to improve the reliability, and thus confidence, in the measurement.

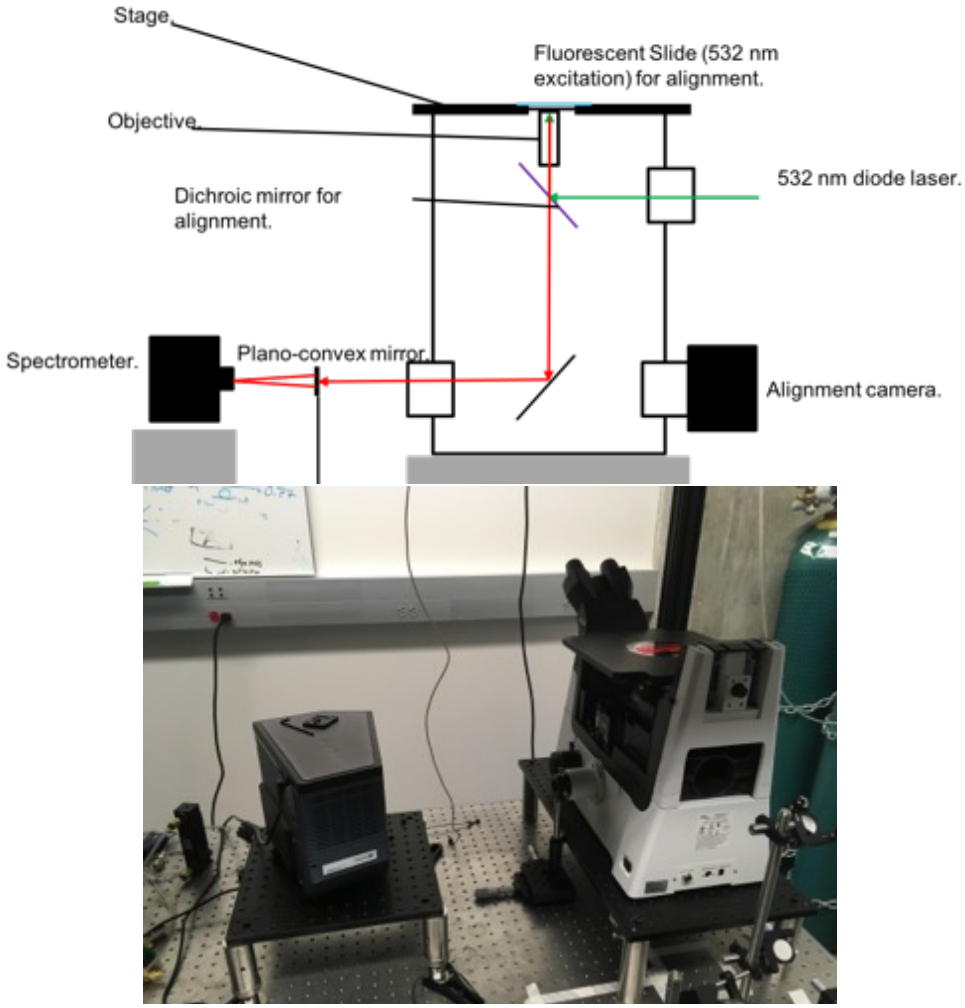


Figure 4. New auto-fluorescence measurement apparatus. (top) Schematic of the auto-fluorescence measurement system consisting of an inverted microscope redirecting the fluorescence into an adjacent spectrograph using free air coupling. For alignment and characterization, a fluorescent glass slide is placed where the plasma-liquid cell would be. (bottom) Photograph of the new system include a Nikon inverted microscope and FERGIE spectrometer with the pink fluorescent glass slide visible on the microscope for alignment.