Raman Path for Generation of Singlet Oxygen in Aqueous Environments

Aristides Marcano Olaizola,[1] David Kingsley,[2] Robinson Kuis,[3] and Anthony Johnson[3]

[1] Division of Physics, Engineering, Mathematics, and Computer Science, Delaware State University, 1200 North DuPont Highway, Dover, DE 19901, USA
[2] Food Safety and Intervention Technologies Research Unit of the United States Department of Agriculture, Agriculture Research Service (USDA ARS), Delaware State University, 1200 North DuPont Highway, Dover, DE 19901
[3] Center for Advanced Studies in Photonic Research, University of Maryland Baltimore County, 1000 Hilltop Circle, Baltimore, MD 21250

Abstract: We propose that Raman excitation can generate singlet oxygen in water environments without the intervention of photosensitizers. Preliminary Raman experiments using continuous-wave laser light at 405 nm validate the hypothesis.

OCIS codes: 350.5130, 300.6540, 170.5180

1. Introduction

Singlet oxygen ($^1O_2$) is the lowest excited electronic level of the molecule of oxygen. $^1O_2$ is highly electrophilic. It can take pairs of electrons of covalent bonds leading to the breaking of complex organic molecules. Singlet oxygen plays a crucial role in reactions of biochemical importance, ruling the conditions for cellular death and life. $^1O_2$ -molecule has been used for disinfection purposes, inactivation of viruses and bacteria, photodynamic therapy of cancer, among other remarkable applications. Figure 1-left shows a simplified scheme of the lowest electronic levels of the molecule of oxygen. The symbol $a^1\Delta_g$ represents the $^1O_2$ -state. The level is located at 0.97 eV from the ground level ($X^3\Sigma_g$), corresponding to the energy of an infrared photon at 1269 nm. The symbol $b^1\Sigma^+{}_g$ corresponds to the second-lowest excited level. Molecules at $b^1\Sigma^+{}_g$ relax fast toward the $^1O_2$ -level representing an alternative path for its generation.

The levels exhibit a complex rotational-vibrational structure not shown in the figure. Quantum Mechanics forbids one-photon direct transition from ground to both states. Researchers use photosensitizers for effective $^1O_2$–photoproduction. The use of these chemical enhancers may generate undesirable secondary effects. Therefore, it is crucial to investigate other ways for $^1O_2$ -generation without the use of photosensitizers. We propose a Raman path to achieve this goal. Raman is a two-photon process where the excitation light generates a Stokes photon of less energy and a transition from ground to an excited state. Quantum Mechanics selection rules allow the Raman transition with high probability. Figure 1-left also shows the Raman paths for excitation of the $^1O_2$ -state. An excitation photon at 405 nm produces a Stokes photon at least at 595 nm. Thanks to the additional vibrational levels, Stokes-photons of less energy are possible. Stokes-photons in the infrared (863 nm) can excite the $b^1\Sigma^+{}_g$ state. We investigate the Raman generation of $^1O_2$ in water and heavy water (D_2O) without the presence of photosensitizers or any other chemical enhancer.

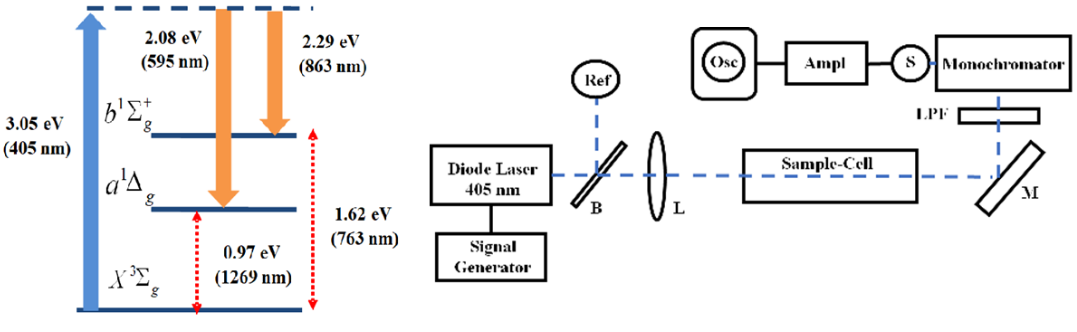


Figure 1: Left - Schematic of the lowest electronic levels of the molecule of oxygen showing the Raman transitions. Right – Home-made longitudinal Raman spectrophotometer.

2. Experiment

We conduct Raman experiments in pure distilled water and heavy water in the longitudinal directions. Figure 1-right shows a schematic of our homemade longitudinal Raman spectrophotometer. A 30-cm long glass cuvette contains the samples. As a reference, we use a similar cuvette containing air. We use a 6-W continuous wave (CW) diode laser at 405 nm (CNI laser) as excitation. We electronically modulate the laser at a low frequency (8 Hz) using a signal generator. A beam-splitter (B) selects a small portion of the light sending it to a reference detector (Ref). A 40-cm focal length lens (L) focuses the light into the samples. Behind the sample-cuvette, we use a long-pass filter (LPF) with a switch-on wavelength at 450-nm. The filter substantially reduces the excitation light. The signal is then redirected toward a double-grating monochromator (260 Cornerstone, Newport). The spectral resolution is approximately 3 nm. The monochromator performs scanning in the region 450-800 nm. In the output of the monochromator, a diode detector collects the signal. A current pre-amplifier amplifies the signal before sending it to a digital oscilloscope for averaging. Finally, we divide the samples' spectra over the spectra recorded for the reference. The procedure eliminates parasitic signals, which may distort the results.

3. Results and Analysis

Figure 2 shows the Raman spectra from water (left) and heavy water (right) after normalization over the reference. Despite the level of noise, we still detect some Raman peaks. The figure identifies three peaks at 605 nm, 658 nm, and 800 nm, observable for both water and heavy water samples. The peaks are clearer for D_2O. The results correspond to the possible Raman response from the molecules of oxygen dissolved in the solvents.

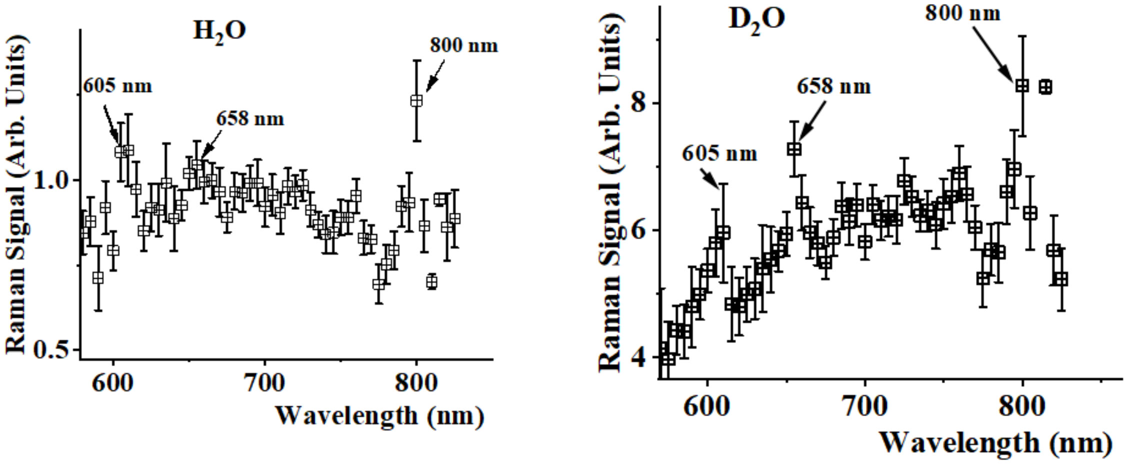


Figure 2. Right the Raman spectrum from a 30-cm column of water. Right the Raman spectrum from a 30-cm column of heavy water.

Conclusions

We describe a ${}^1O_2$ –state excitation path based on Raman transitions from the ground state generating Stokes-photons in the visible region of the spectrum. To test the prediction, we conduct Raman spectroscopy in the longitudinal direction for distilled water and heavy water in a 30-cm pathlength glass cuvette.

Acknowledgements

The authors acknowledge the support of the National Science Foundation (Award 1831332) and the United States Department of Defense (Award 78038-RT-REP).

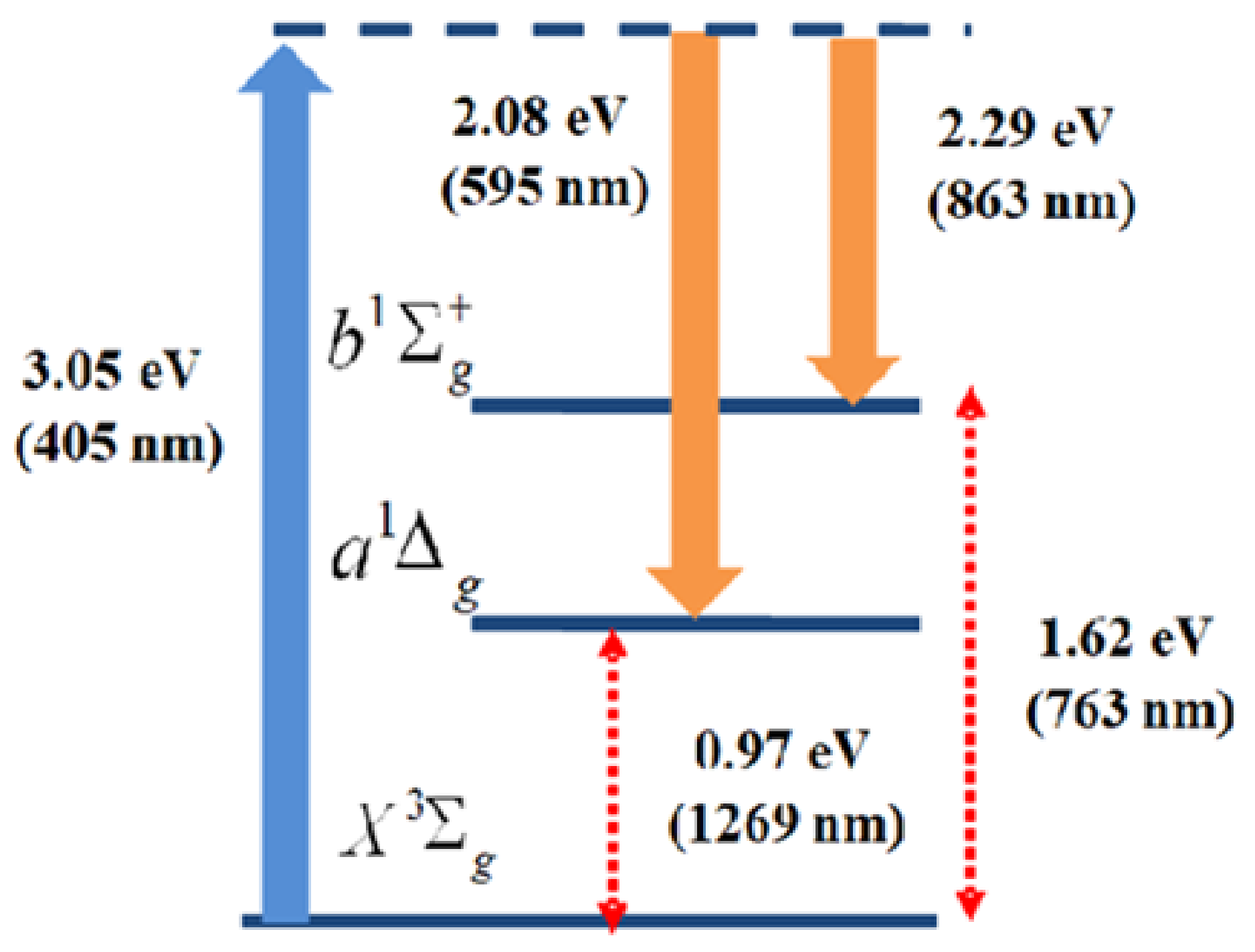
Raman Path for Generation of Singlet Oxygen in Aqueous Environments

Aristides Marcano Olaizola,[1] David Kingsley,[2] Robinson Kuis,[3] and Anthony Johnson[3]

[1] Division of Physics, Engineering, Mathematics, and Computer Science, Delaware State University, 1200 North DuPont Highway, Dover, DE 19901, USA
[2] Food Safety and Intervention Technologies Research Unit of the United States Department of Agriculture, Agriculture Research Service (USDA ARS), Delaware State University,
[3] Center for Advanced Studies in Photonic Research, University of Maryland Baltimore County, 1000 Hilltop Circle, Baltimore, MD 21250

INTRODUCTION

Singlet oxygen ($^1O_2$) is the lowest excited electronic level of the molecule of oxygen. $^1O_2$ is highly electrophilic. It can take pairs of electrons from covalent bonds leading to the breaking of complex organic molecule. Singlet oxygen plays a crucial role in reactions of biochemical importance ruling the conditions for cellular death and life. $^1O_2$-molecule has been used for disinfection purposes, inactivation of viruses and bacteria, photodynamic therapy of cancer, among other remarkable applications. Quantum Mechanics forbids direct one-photon excitation of the $^1O_2$-level. Researchers use photosensitizers for effective $^1O_2$–photoproduction. The use of these chemical enhancers may generate undesirable secondary effects. It is crucial to investigate other ways for $^1O_2$ -generation without the use of photosensitizers. We propose a Raman path to achieve this goal. Raman is a two-photon process where the excitation light generates a Stokes photon of less energy and a transition from ground to an excited state. Quantum Mechanics selection rules allow the transition with high probability. We research the Raman generation of $^1O_2$ in water and heavy water without the presence of photosensitizers or any other chemical enhancer.



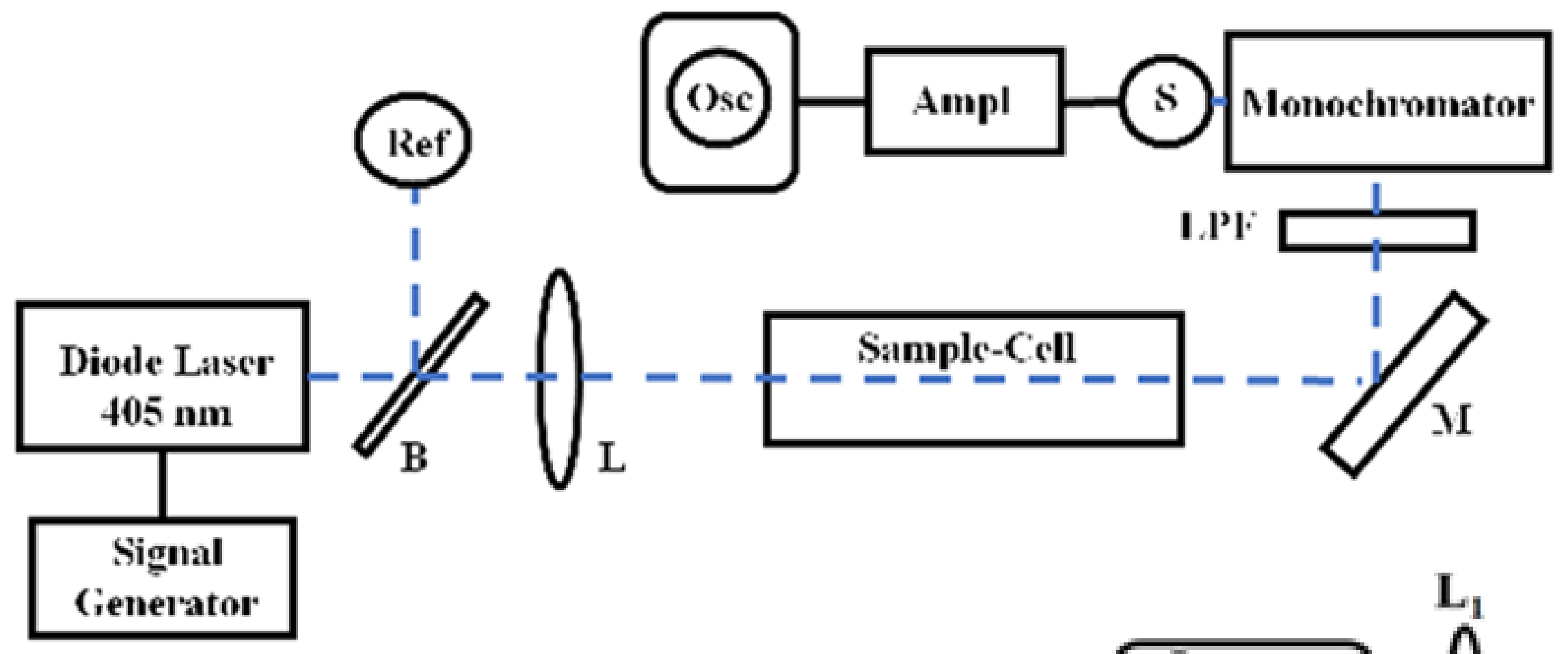
Schematic of the lowest electronic levels of the oxygen molecule showing possible Raman transitions.

An excitation photon at 405 nm produces a Stokes photon at least at 595 nm. Thanks to the additional vibrational levels, Stokes photons of less energy are possible. Stokes photons in the infrared (863 nm) can excite the $b^1\Sigma^+_g$ state. When pumping at 405 nm the expected $^1O_2$ -Raman lines should comply with the equations

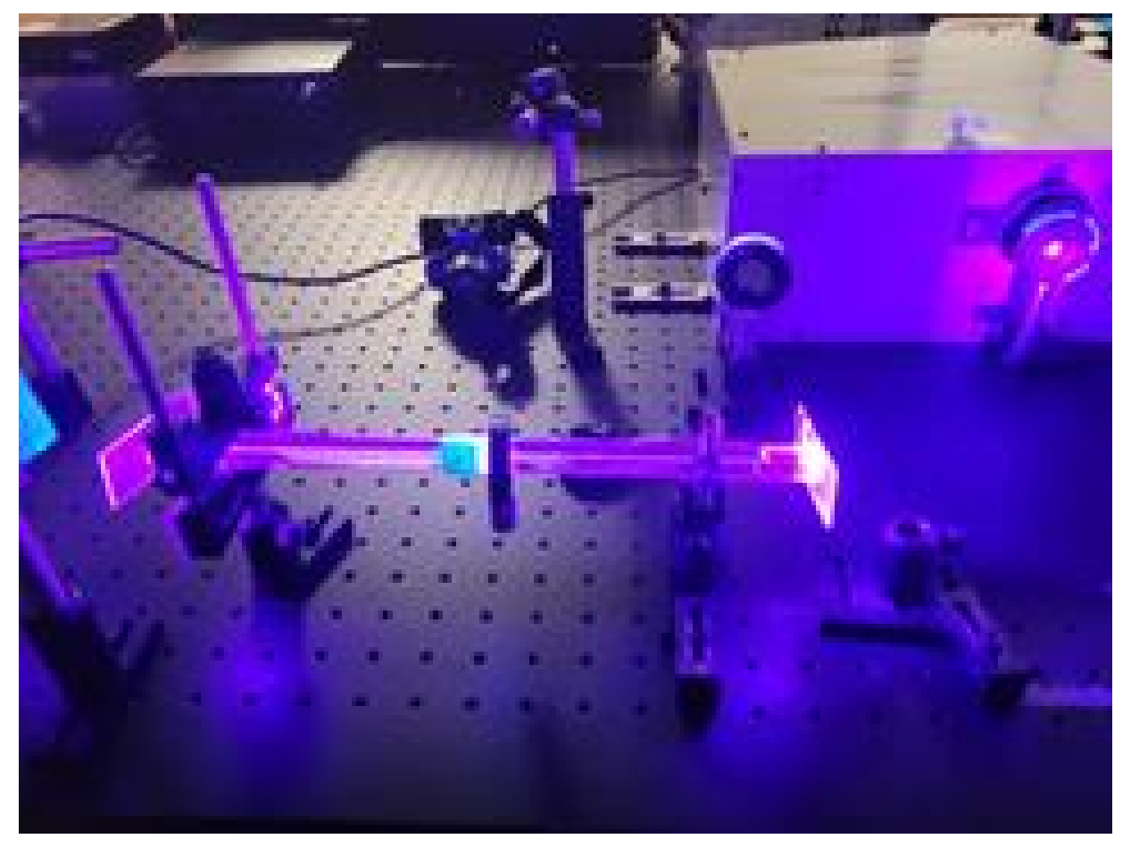
$$\frac{1}{\lambda} > \frac{1}{405\ nm} - \frac{1}{1269\ nm} \quad \text{or} \quad \frac{1}{\lambda} > \frac{1}{405\ nm} - \frac{1}{763\ nm}$$

Expected Raman lines at 595 nm and 561 nm when pumping at 405 nm.

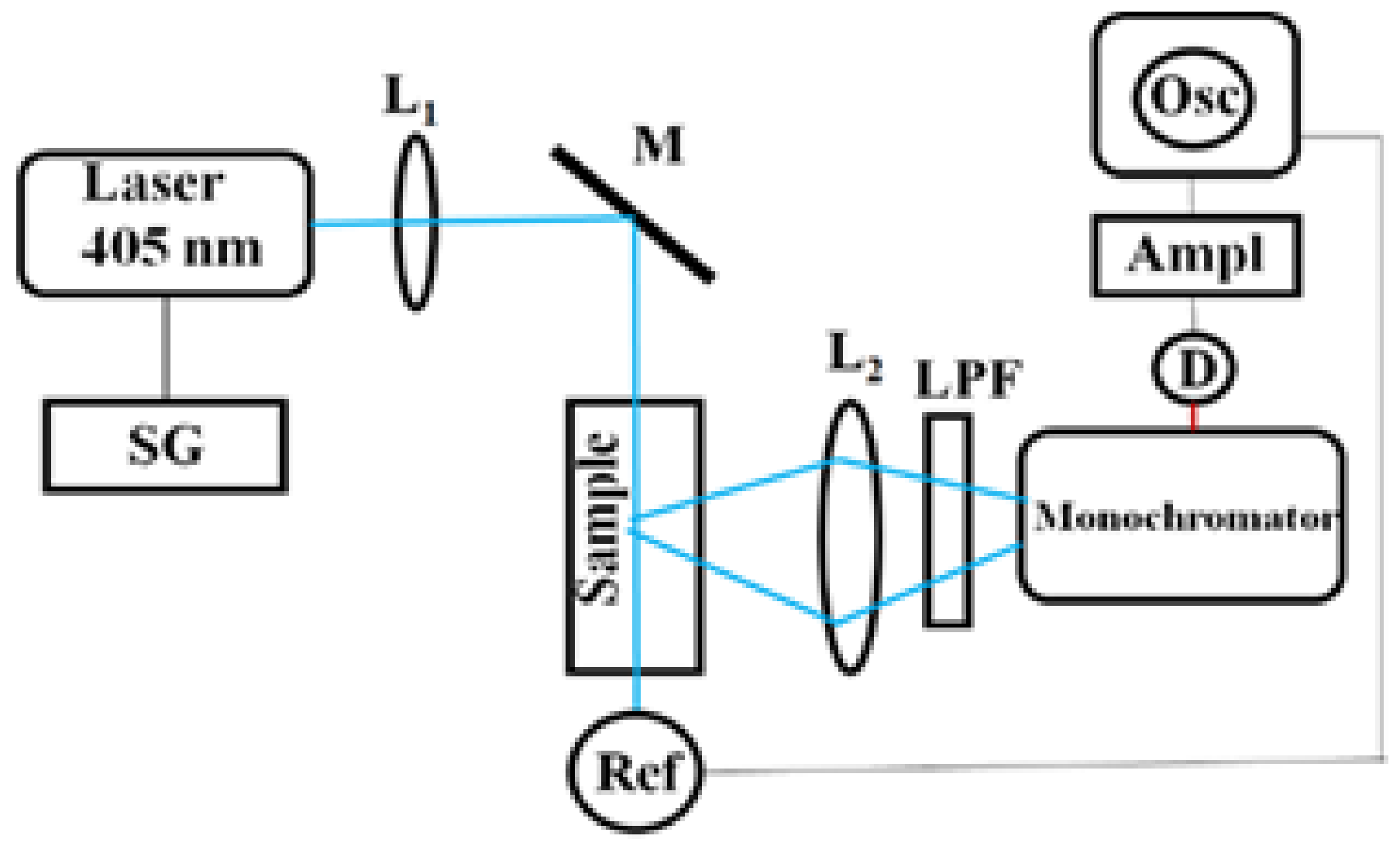
EXPERIMENT



Raman 0° experiment



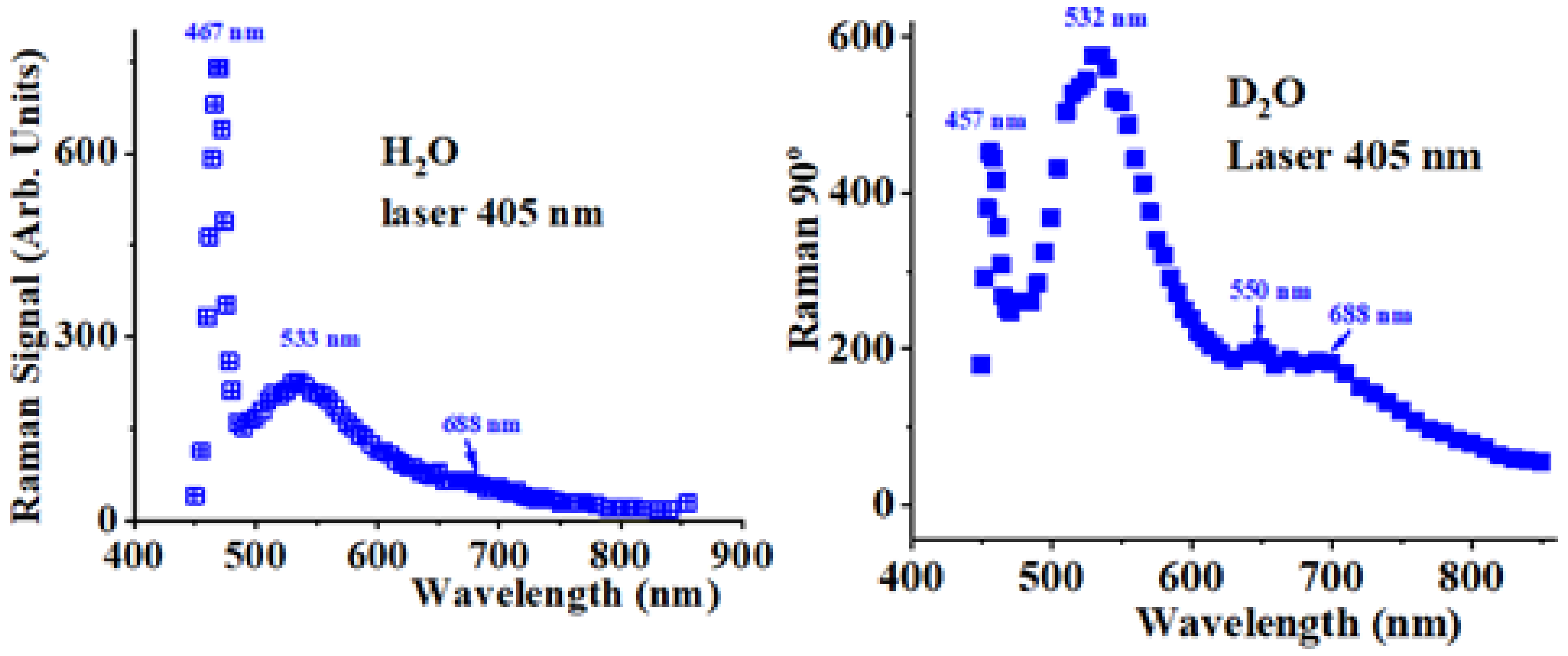
30-cm home –made cuvette



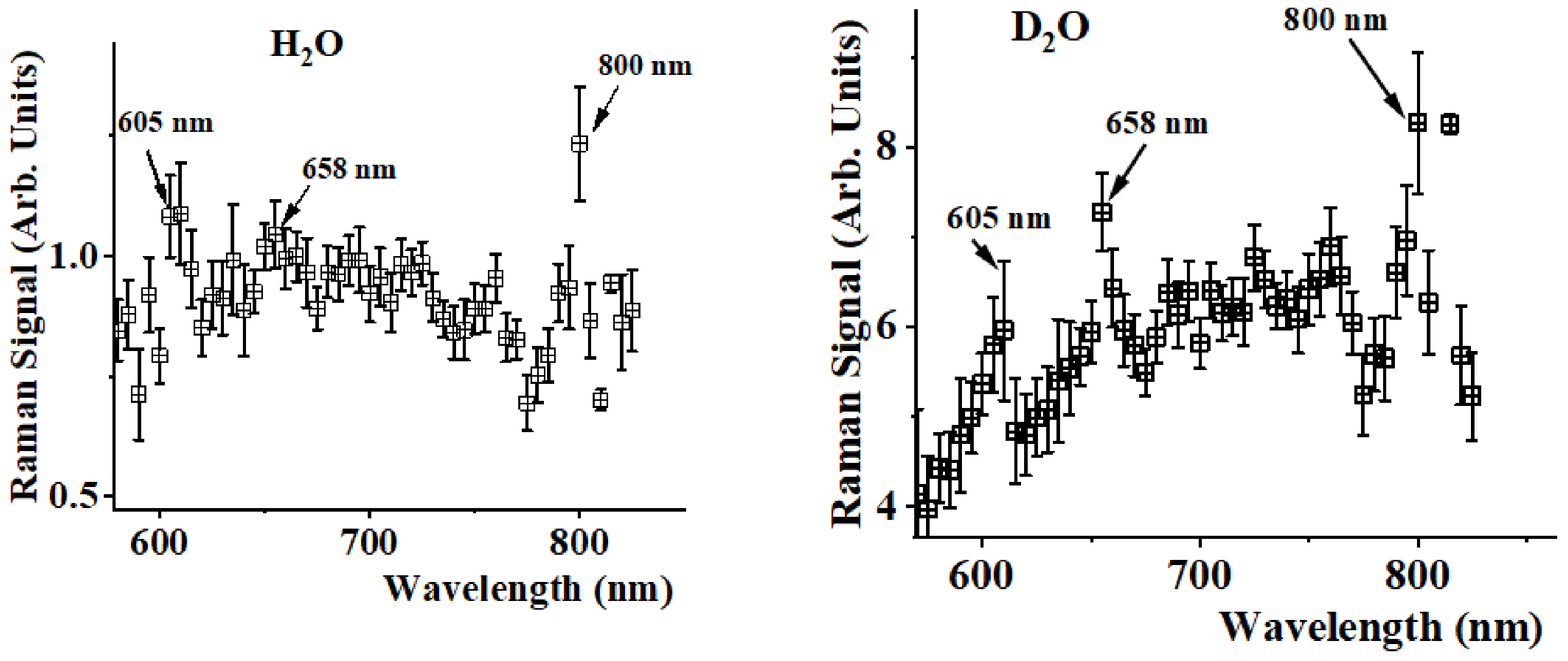
Raman 90° CW experiment

RESULTS AND ANALYSIS

CW 90° Raman experiment

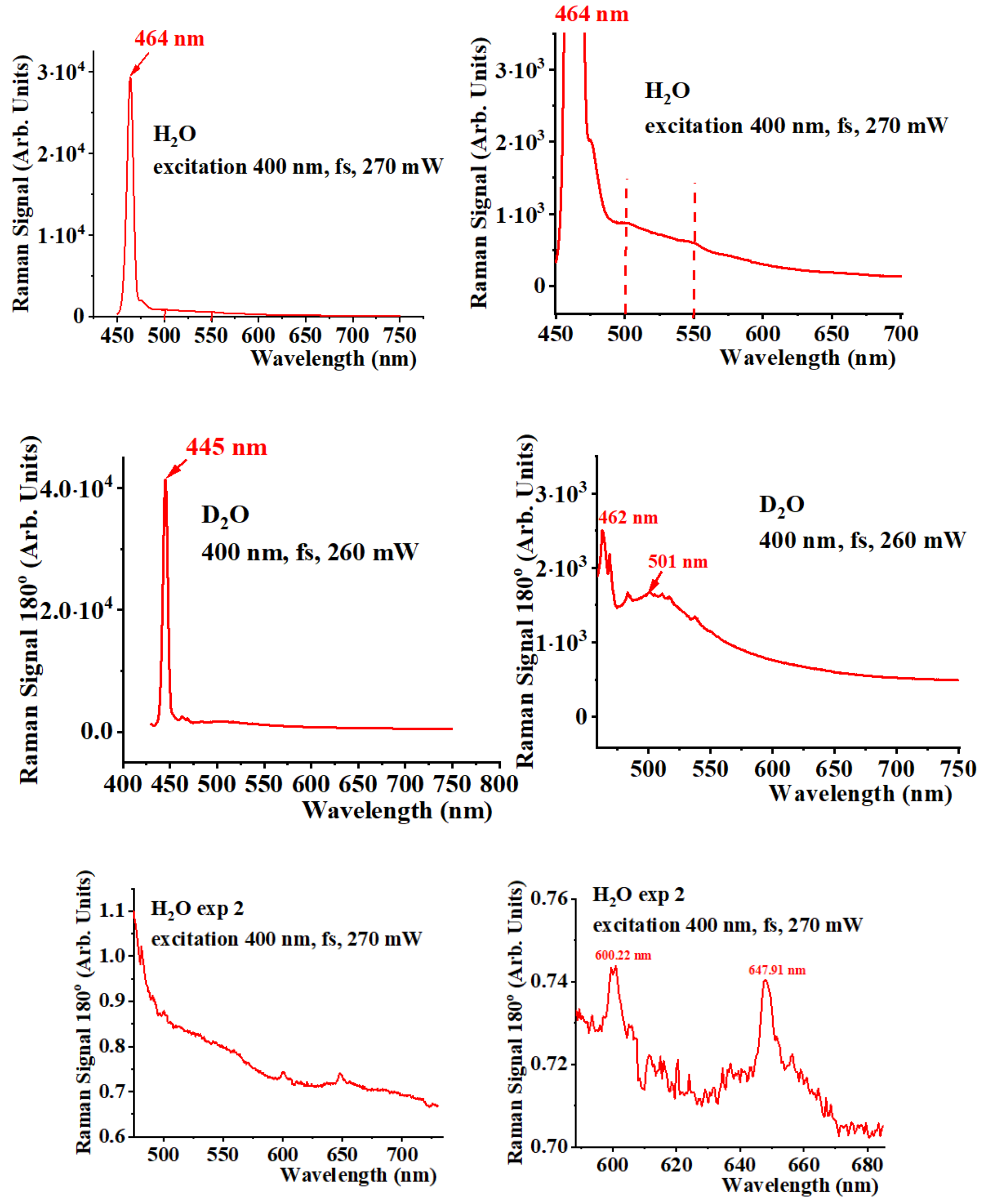


Raman 0° CW experiment



RESULTS AND ANALYSIS

Femtosecond 180° Raman experiment



CONCLUSIONS

We have conducted Raman experiments on water and heavy water in 0°, 90°, and 180° degrees experimental configurations using CW and fs-laser sources in the blue spectral region (400-410 nm).
We obtain a clear Raman peak, which corresponds to the stretching Raman mode of the solvent molecules. The peak can be used for calibration purposes.
We have obtained much smaller Raman peaks in the red region of the spectrum (> 600 nm) which may be associated to the Raman generation of singlet oxygen.

ACKNOWLEDGEMENTS

We acknowledge the support of the National Science Foundation (NSF award 1831332) and the Department of Defense (DOD Application No. 78038-RT-REP).