Blending teaching and research: Low-cost surface-enhanced Raman scattering to probe the reaction dynamics of a molecular photoswitch

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Introduction

Research and modern experimental techniques are becoming increasingly important in undergraduate science education, even at small liberal arts institutions like MidAmerica Nazarene University. These programs often need the flexibility of instrumentation that can be utilized in multiple courses. Instrument cost is also a concern. This project is addressing these needs in the area of physical chemistry/AMO physics.

In addition to research done in collaboration with the Elles group, at MNU this project affects the following courses:

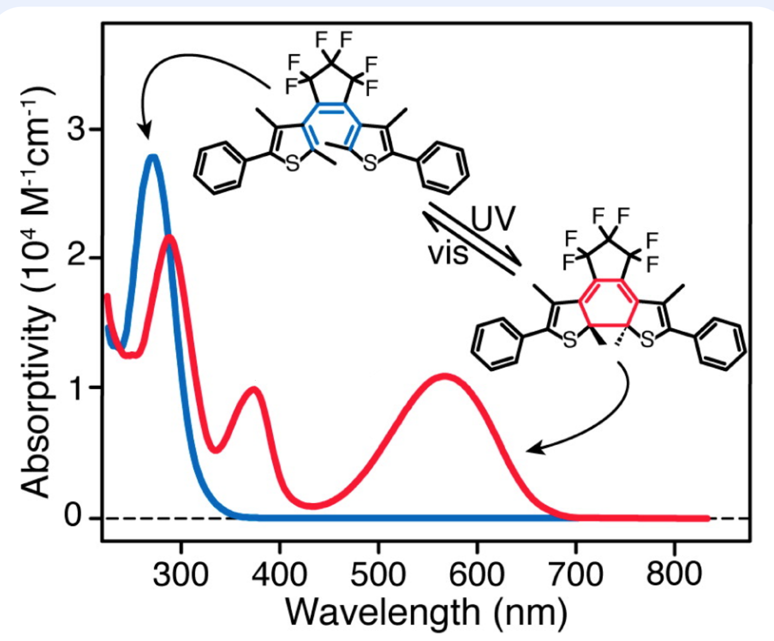
- **Quantum Chemistry** - currently no lab. A Raman spectroscopy activity and a nanoparticle colloid synthesis activity will be added Fall 2017.
- **Analytical Chemistry** - Raman spectroscopy will be introduced as a modern analytical technique Spring 2017.
- **General Physics** - currently no “hands on” laser use. Due to the flexible and portable design, the experimental setup from this project will also be used for interferometry and optics activities.

Diarylethene Photoswitch

Diarylethenes (DAE) change color upon absorption of light via controllable, reversible photoisomerization. They are also thermodynamically stable. These features make DAE molecules particularly interesting as photoswitches or optical storage devices. Understanding the photochemistry of the isomerization reaction is crucial for developing future applications of these molecules.

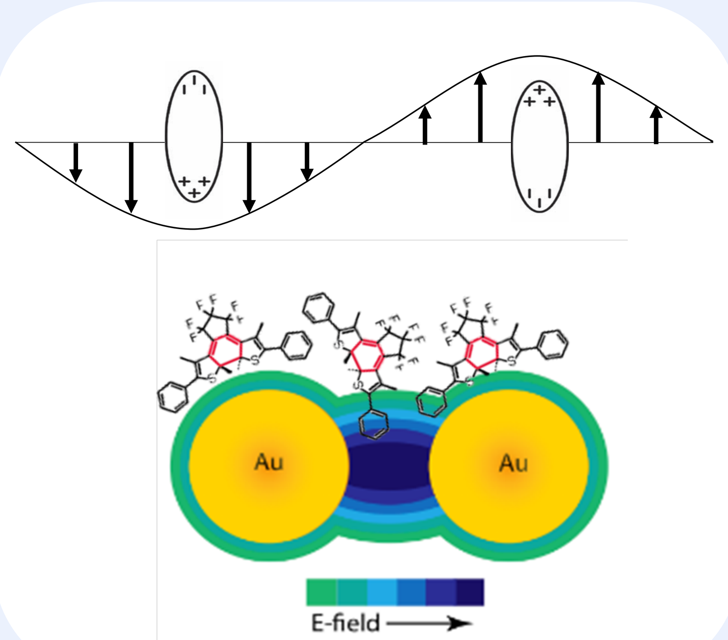
Blue curve:
open (colorless) isomer

Red curve:
closed (colored) isomer



J. Phys. Chem. A, **2014**, *118* (43), pp 10011-10019

Enhanced Photoswitching

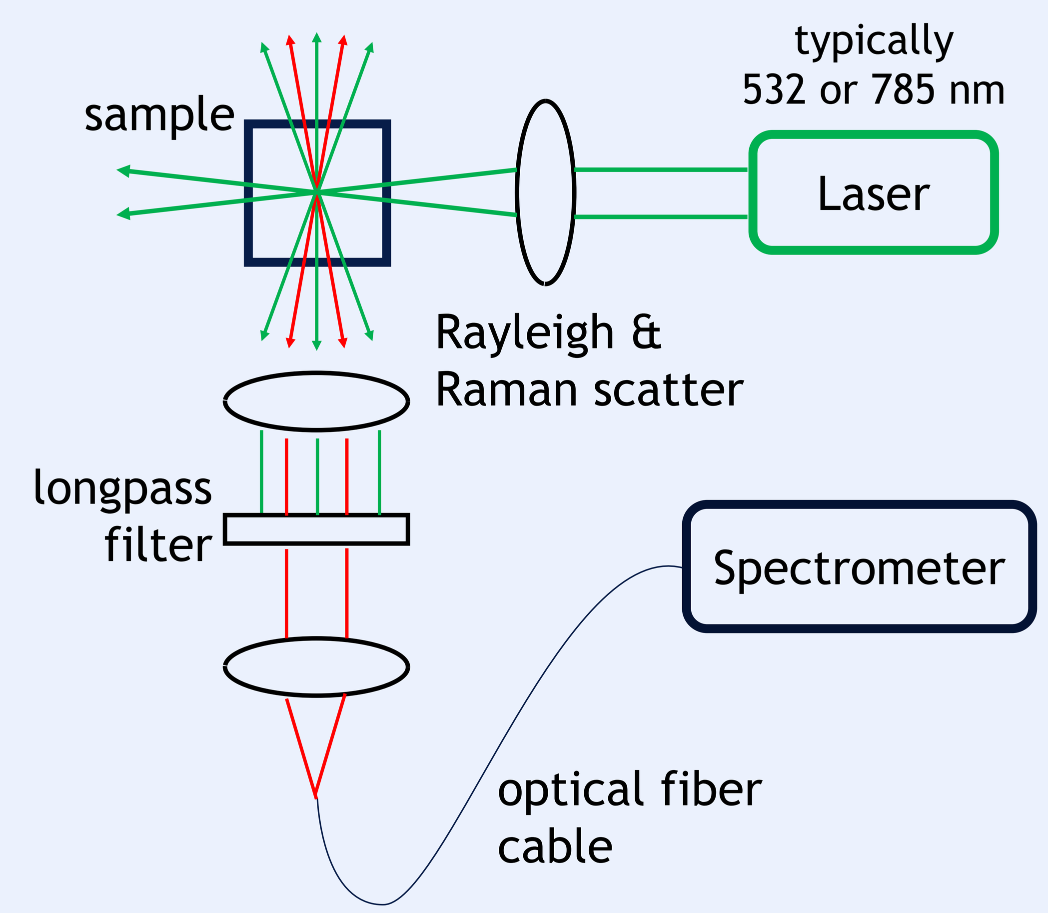


The Elles group is currently studying the effect of non-resonant field enhancement (due to surface plasmons) on the behavior of the photoswitch.

An important aspect to this investigation is finding a suitable way to probe only those molecules close to the gold nanoparticle surfaces since enhancement is most pronounced in the gap.

Surface-enhanced Raman spectroscopy may be that probe.

Raman Setup



Experimental Design

A Raman scattering experiment has three component parts:

1. a laser light source that is stable and has a narrow bandwith,
2. probe optics to efficiently collect the scattered light, and
3. a sensitive detector with adequate resolution.

Each of these components are being optimized for cost and open, modular design that allows for curricular flexibility and the opportunity to discuss instrument design with students. As a reference, a typical commercial Raman instrument costs approximately $15,000.

To date, the following components have been used to build the low-cost Raman/SERS instrument:

Laser ($100-200)
- 532 nm (Thorlabs CPS532, 4.5 mW, $159)
- 780 nm (Thorlabs CPS780S, 4.5 mW, $98)
- 785 nm (Coherent Mantis seed laser, 100-300 mW, at KU)

Collection optics (~$750)
- ½” lens tube with 15 mm focal length lens
- longpass filter with sharp cutoff just after Raman wavelength
- lens to couple collected light to a fiber optic cable
- 2D translation stage for precise positioning

Spectrometer ($3,000-6,000)
- StellarNet BLUE-Wave minature fiber spectrometer ($2700)
- StellarNet BLACK-Comet spectrometer ($3000)
- StellarNet Raman High Resolution TEC spectrometer ($5300)

So far initial experiments have yielded Raman spectra using the more expensive Mantis laser, but not yet with the lower cost 4.5 mW laser sources. A laser source with intermediate power and cost may also be investigated because commercial SERS substrates require less laser power due to the field enhancement of the metal nanoparticles.

Nanoparticles & Surface-enhanced Raman

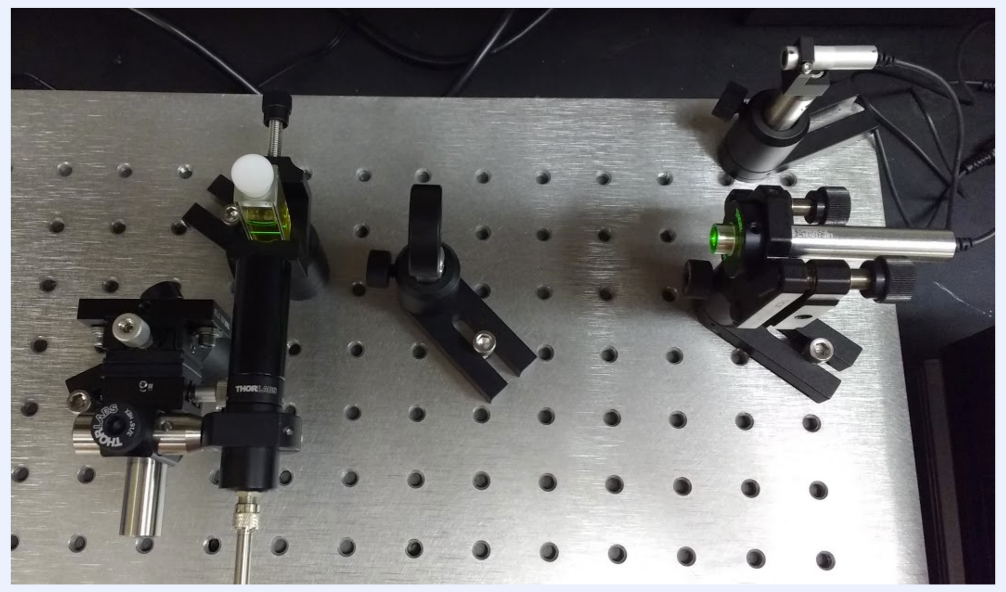
Surface-enhanced Raman spectroscopy (SERS) can be done using:

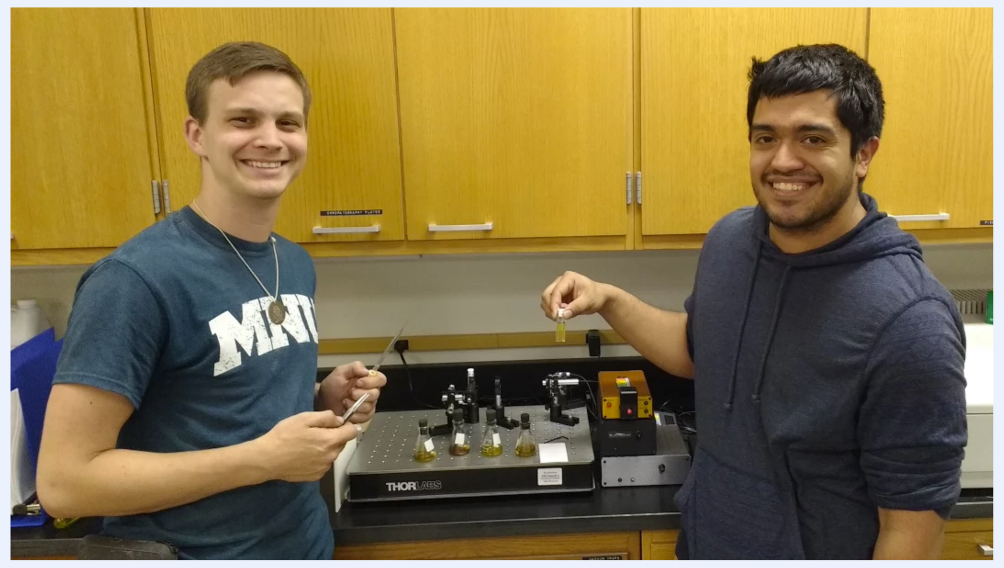
- metal nanoparticle colloids (primarily Ag and Au)
- roughened metal surfaces
- nanostructured metal surface (most common)

While commercial SERS substrates can be purchased, they would most likely be cost-prohibitive for teaching laboratories. However, future work on the diarylethene photoswitch will involve SERS substrates and possibly a plasmonic array.

Currently, the focus of the MNU group is on colloidal metal nanoparticles that can be synthesized using common chemicals.[1] After observing SERS in the liquid system, the next step will be to lay down nanoparticle layers on glass substrates for SERS measurements. The goal will then be to successfully observe photoswitching behavior on a surface coated with nanoparticles.

[1]Jason Cooke, Dominique Hebert, and Joel A. Kelly *J. Chem. Educ.*, **2015**, *92* (2), pp 345-349





MNU students Timothy Myers (left) and Jesus Villa (right) are synthesizing silver nanoparticles and setting up the Raman instrument (above).

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