



Intern Final Report

August 2023

Changing the World's Energy Future

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Time-Gated Raman Spectroscopy: Intern Final Report

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Abstract:

Time-gated Raman spectroscopy is a powerful tool for rapid non-destructive analysis of chemical compounds, particularly when combined with other investigative methods. Time-gating the signal obtained from a sample during Raman spectroscopy allows for the removal of background emission and black body radiation, improving clarity and accuracy of scans. The main objectives of this project were to prove the lab's time-gated Raman spectroscopy system works as proof of concept and to make select improvements to the in-house LabVIEW software used to run the time-gated system. This time-gated system will be added to the CTK's TAP reactors in the future, but this is out of the scope of this internship project. This research is important, as understanding the mechanisms behind catalysts leads to designing better systems/materials and the perfection of catalysts, and energy-efficient chemical manufacturing is key when designing a greener future. The research for this project was done with samples at both ambient conditions in sample holders and at operando conditions (i.e., high temperature, unsteady-state) inside a small-volume chemical reactor. Numerous spectro-kinetic scans of the catalysts were obtained, but the advanced dynamics of these systems are still being interpreted. There is data that demonstrates that the time-gated system is correctly rejecting emission from samples, and one can observe real-time changes in the signal from the sample, due to coking or changes induced by redox chemistry. Chemical manufacturers and the planet are the main beneficiaries of catalysis research, as better catalysts will reduce carbon emissions.

Time-Gated Raman Spectroscopy: Intern Final Report

Introduction

Raman spectroscopy is the method of analyzing the inelastic scattering of light off a sample. This can tell you information about the structural information of the compound and can be used as chemical “fingerprint”. Time-gating allows for the rejection of confounding signals caused by photoluminescence and black body radiation. Raman scattering is due to interactions of the incident photon with the vibrational and rotational characteristics of the compound and is essentially instantaneous, as opposed to long lifetimes caused by photoluminescence. Therefore, time-gating the detector allows for only Raman scattered photons to be collected, improving signal clarity and accuracy of information. In a chemically active system such as a chemical reactor, being able to accurately identify structural changes to the compound in real-time is invaluable.

I did not have a huge interest in optical physics and had no knowledge of Raman spectroscopy before the internship, but I am about to enter my senior year of chemical engineering at Montana State University and an internship in a catalysis lab is a natural match. I am interested in green energy, and many of the catalyst samples analyzed facilitate dehydrogenation reactions that produce hydrogen gas that could be used for that purpose. Regardless of my interest coming in, I found this project to be enjoyable to work on and interesting.

Description of the Research Project

As preface, while Dr. Fushimi is the overall head of the research group and listed mentor in the internship agreement, Dr. Malizia was my day-to day mentor overseeing my work and participation. This project's purpose was a proof of concept on the lab's time-gated Raman spectroscopy system and to improve the in-house LabVIEW program used to run those spectroscopy experiments. In addition, collection of mass spectrometer, emission, and photon lifetime data was used for supplementary characterization. To achieve this purpose, the same catalyst sample was scanned using the existing commercial Raman system and the time-gated Raman system, under the same conditions and integration times, and then the two scans were compared to each other. If the time-gated system is successful, it will remove all signal not associated with Raman nodes, and ideally have better signal-to-noise ratio.

This project combined qualitative and quantitative analysis. For data collection, both the normal and time-gated Raman systems took spectrum scans of a catalyst sample at certain benchmark conditions, such as after methane gas flow or after reaching a set temperature. The time-gated system can also collect signal data from a single wavelength/wavenumber over the course of an experiment. Emission data was taken in a similar manner as the Raman data to provide supplementary information. Mass spectrometer data was also taken continuously during operando experiments. For analysis, Raman and emission spectra and mass spectrometer data were plotted in Excel. Meanwhile, signal scans of one wavelength over time from both time-gated Raman and emission were processed using MATLAB. In MATLAB, the mean values of the scans were taken and plotted against time as the experiment progressed.

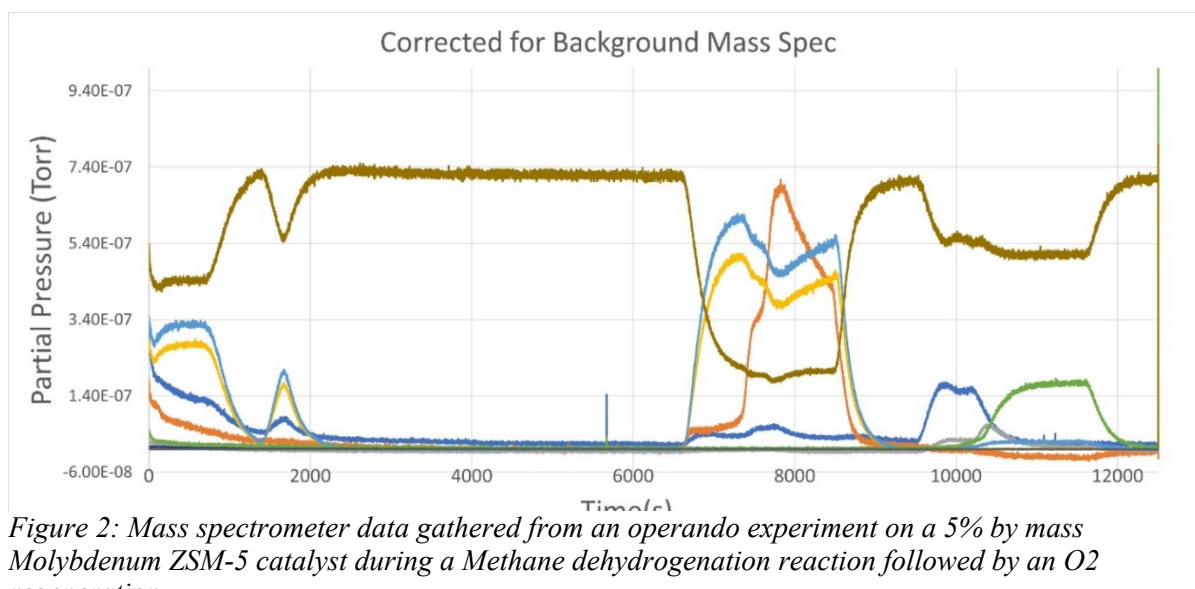
Figure 1 illustrates the efficacy of the time-gated system at removing the emission from a chromia catalyst. This is shown by the lack of signal to the right of the Raman node (550 cm^{-1}) in the time-gating signal when compared to the commercial. This does prove that the time-gated

Raman system is working as intended and superior to the commercial in terms of quality. Even though the emission near the chromia catalyst's Raman band is weak, other catalysts that have stronger photoemission will benefit greatly from the time-gating.

Emission from
sample



Figure 1: Data collected from the same chromia catalyst sample under similar integration times from both the time-gated and commercial system. The Raman node at 550cm^{-1} is due to Cr^{3+} and can be tracked during redox reactions.



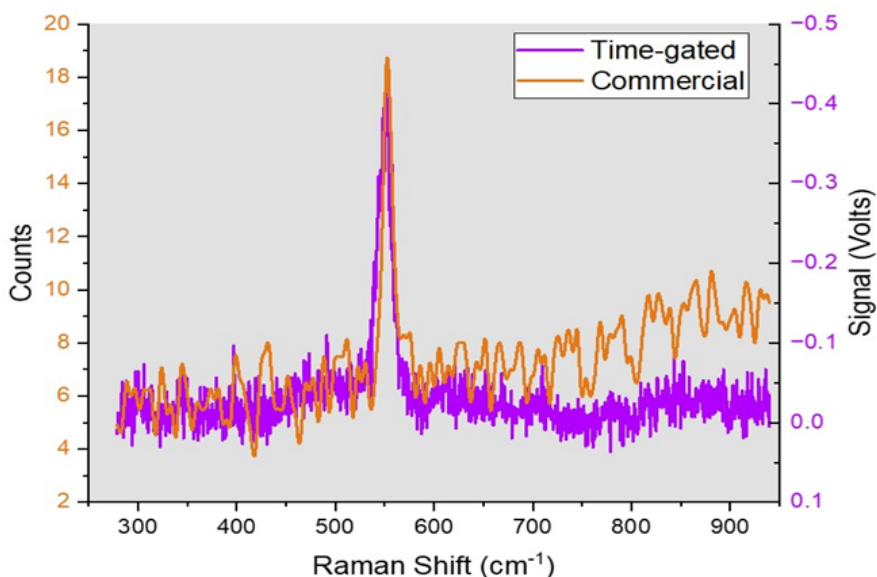


Figure 2 shows mass spectrometer data from an operando experiment on a molybdenum ZSM-5 catalyst, allowing for the tracking of chemical products. For example: during the time interval of [6,500; 9,000] we can see H_2 production when the catalyst is exposed to methane gas, showing that a dehydrogenation reaction is proceeding as expected. Some CO is also produced from oxygen contained in the catalyst, but it is inferred here (and supported by the lowering in emission signal during this experiment) that some carbon is deposited on the surface of the catalyst, instead of leaving the system as CO or unreacted CH_4 . This surface carbon is shown leaving the system during the time interval [9,500; 11,500] range as the catalyst is exposed to oxygen gas that rips the carbon off as CO and CO_2 and regenerates the catalyst. Once this reaction reaches its completion, we can see the partial pressure of O_2 rise until the Argon purge at time 11,500. The reaction should also be producing benzene, but it most likely condensed into a liquid after leaving the reaction chamber and did not reach the mass spectrometer. The mass spectrometer data from this experiment was interesting but is only supplemental to the spectroscopy data.

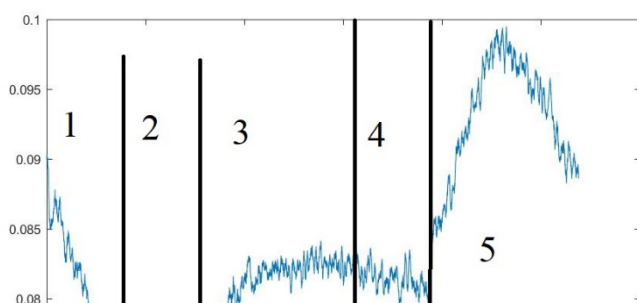


Figure 3 exemplifies data from a time-gated Raman scan of a single wavenumber on a

Figure 1: Complete exothermic shift of 448.4 cm^{-1} . The x-axis is the signal received during stages 2 and 4 are Ar, stage 5 is cooling of the

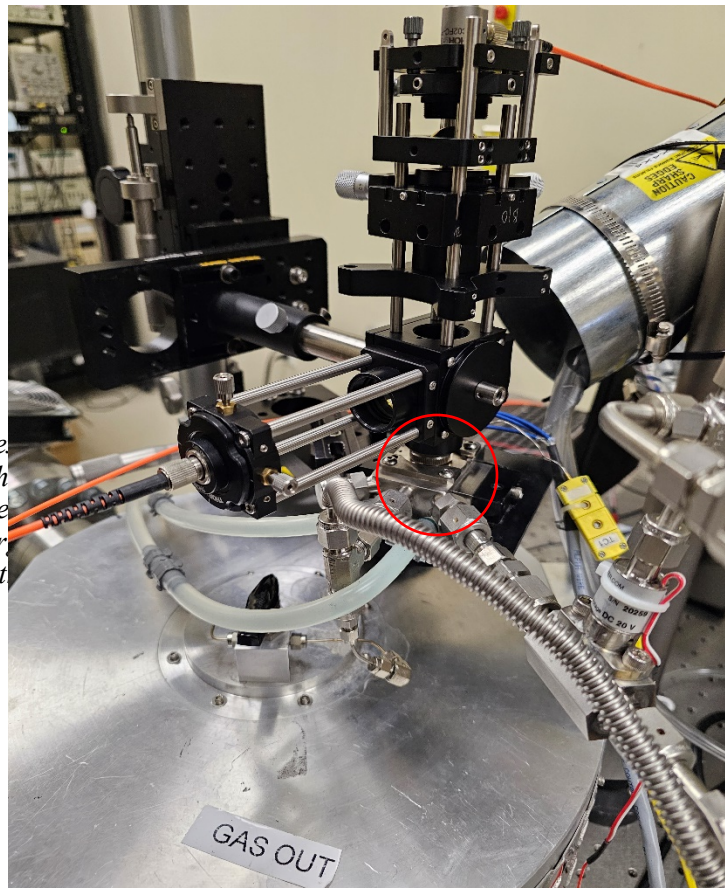


Figure 2: Picture of the Harrick cell taken by Nathan Berquist. This is the reactor used for operando experiments. The top fiber optic, colored orange, carries photons coming from the reactor, the bottom fiber optic carries the laser light in. The Harrick cell has a red circle around it and is where the sample is located.

nickel-ceria-zirconia catalyst. We can track the drop in signal from carbon deposition from methane flow during stage 1 and subsequent rise in signal from carbon removal during stage 3. This technique can directly monitor catalyst condition, as opposed to inferencing it from mass spectrometer data.

Contributions Made to the Research Project

For most of the internship, whenever we ran experiments, I activated the interlock system, turned on the lasers, and operated the software collecting the spectroscopy data. My mentor, Dr. Malizia to be specific, would make alignment changes to the laser and operate the gas flow and mass spectrometer software. I created the plots obtained from experimental data, using Excel and MATLAB as necessary, some of which are in the previous description section.

Significant contributions I made to this project are the changes I made to the in-house LabVIEW code used to run time-gate Raman scans. For context, LabVIEW is a programming language made for non-programmers with popularity in research settings due to its easy integration with National Instruments hardware. The main complaint with time-gated LabVIEW program was the save file system. The original method had a hard-set folder path and checked the current time and used the day, month, and year to check/generate a folder (e.g., 06-13-2023). Then the code used the hour, minute, and second to name the file generated for each scan (e.g., 171356 for 5:13:56 PM). This system did not allow for user input to change the folder or file name and could be confusing to sort through files when running through subsequent experiments. This system also used a “Write to Spreadsheet” function that was no longer supported and was messing up data due to a bug.

My mentor wanted a system where the operator sets the folder and filename and to have filename iterate sequentially as scans are generated. With the goal of keeping the code simple, I used LabVIEW’s “Write to Measurement File VI” (Virtual instrument; a program, sub-program, or function in LabVIEW) which natively allows one to set the file type, how files are separated, how they’re named, among many other parameters. This also allows for a control on the front panel that opens the file browser and allows you to pick/create the folder and base filename and then displays the subsequent folder path on the panel. The initial parameters I set tell the

subprogram to check the filename, which you pick before the experiment, and then iterates the next available filename if it already exists. The filenames now look like: H2Test_00001, H2Test_00002, etc. This subprogram also allows for fine control over how data is saved, such as segmenting, file size limits, headers, etc. I also chose this VI not just because of its configurability, but also because it is easy to understand and replace in the future. I also figured out how to do this by writing a sub VI from scratch.

The program also offers a function to display the real-time value of the detectors or scans using a separate, and initially unlabeled, start/stop button system. The problem was that it was not obvious when this functionality was operating, and telling the program to run an experiment scan while this was operating crashed the whole program. I implanted a one-button system, where the “Real-Time Scan” button turns red once clicked and tells the operator that this function is running and to hit the button again to stop it. I also made the experiment scan button become greyed-out and disabled while the real-time scan is running, and vice-versa, to eliminate the possibility of inexperienced operators inadvertently crashing the program.

I also changed the way that operando time-gated program would display data. Initially, the program would display a chart after each scan that displayed the signal versus time, essentially showing a scatter of the voltage signal received by the PMT at each time-step. This data was not very legible and was not useful as the average value of the signal during the scan is the important information and is used for post-experiment data workups. To make a more useful chart, I plotted the mean value of each scan versus the scan number. The end result is a continuously updating chart showing the average value of each scan as the experiment runs. This allows for easy monitoring of the Raman peak while the experiment is running, something that used to have only been seen when processing data post-experiment.



Figure 3: Screenshots of the front of the LabVIEW code for the time-gated system. This is still an in-progress system, but most elements have been edited by me.

Skills and Knowledge Gained

Through this internship I was able to learn about Raman spectroscopy, laser safety, programming with LabVIEW, and a basic level of understanding with MATLAB. I will not go

into further detail about Raman spectroscopy here, but as part of INL's onboarding I learned about lasers and laser safety in detail. MATLAB was used to process some of the data obtained from experiments, however most of the functions/scripts were already created so I only needed to learn the basics of navigating MATLAB. I also got some brief experience using Origin, a graphing software, and I wish I had been able to use it more during my time at INL.

The bulk of my learning was on LabVIEW programming, a software I had not heard of before this internship. During my time here I watched many videos on the basics of LabVIEW and saw multiple in-house programs that had been written in LabVIEW. While I am obviously not a master at LabVIEW, through my experience editing the time-gated program (mentioned in the "Contributions" section) I feel as though I have working knowledge of how to write LabVIEW code. Through feedback from my mentor, I also got some experience on designing the aesthetics of the LabVIEW front panel from a user perspective, such as paying attention to color language and presentation of controls.

Research Experience Impact on My Academic/Career Planning

This internship reaffirmed my decision to study chemical engineering, as I feel like it's a field where a lot of my strengths lie. I do not feel like this internship affected my view on research work, as it was about what I expected. Overall, I feel neutral, but I would not mind doing more research work in the future. Talking with members in my research group made me a bit more apprehensive towards attending graduate school. I have no doubt that I could do it if I wanted to, but at the moment I think I am more interested in heading into industry.

Relevance to the mission of DOE

This research, and the greater catalysis lab it's a part of, strongly relates to the DOE's mission in addressing energy and environmental challenges. Catalysts allow for a significant reduction in energy needed for chemical manufacturing, and thus are of great interest in a time where lowering energy-use is prioritized. Some catalysts also offer alternate pathways for a chemical reaction, which can lead to not only lower material use and energy needed for mass separation, but also the avoidance of waste material which could be toxic.

This research project's technique has applications in characterization and monitoring catalyst condition. Real-time changes in the catalyst can be detected quickly and easily via time-gated Raman spectroscopy. Furthermore, many of the catalysts in the lab take part in dehydrogenation reactions which produce hydrogen gas. Hydrogen gas is popular choice for future clean energy generation, and offering more options other than the energy intensive process of recovering hydrogen from electrolysis would help further decarbonize of our grids.

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