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Technology Report

Accessible and Interactive Learning of Spectroscopic Parameterization through Computer-Aided Training

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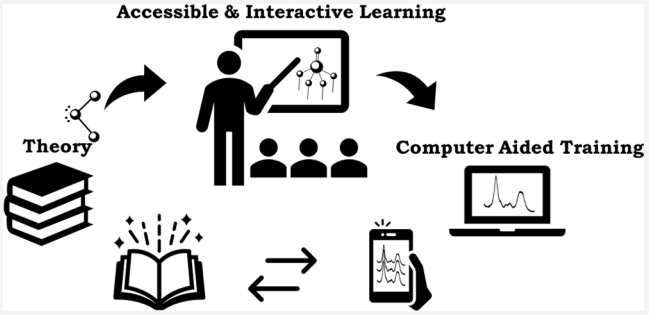
ABSTRACT: The importance of utilizing spectroscopic techniques for unraveling structural and compositional changes in nonreacting and reacting systems is unquestionable. Nowadays, efforts are directed towards the introduction of relevant spectroscopic techniques to undergraduate students in order to prepare them for future careers in industry and academia, where these techniques are becoming ever-more popular for material quality control, reaction monitoring, process control, etc. Educators have increasingly shifted to programming-based lessons due to intrinsic benefits such as improved and broad accessibility over interactive lessons, dual exposure to chemistry and computer science topics, remote teaching, etc. In this work, a MATLAB-based program is built to expose students at higher education levels (undergraduates and graduates) as well as new users to spectral parameter estimation towards the collection of Raman spectra in a timely manner with high signal to noise ratio (S/N). The development of this intermediate-level intuitive understanding in spectroscopic techniques has the potential to serve as the interface between course curricula and hands-on experience in advanced techniques.



KEYWORDS: *Spectroscopy, Computer-Based Learning, Distance Learning/Self Instruction, General Public, Chemical Engineering, Laboratory Instruction, Physical Chemistry*

INTRODUCTION

There is an undoubtable growth in promoting technologically relevant teaching methods in undergraduate course curricula, particularly those including computational and coding skills, in order to facilitate accessible and interactive learning in all relevant topics in which students may not be proficient. Educators need to ensure that any learning sources and educational outreaches are accessible to all students. The recent COVID-19 pandemic encompasses one among many other examples where the lack of in-person teaching may affect the quality of instruction as well as the timely completion of educational activities. On the other hand, it is generally recognized that the inclusion of computational and visualized approaches in tandem with online teaching modules in traditional science and mathematics curricula promotes the next-generation of hands-on engagement with course material that may tend to be abstract and difficult to grasp for some students when presented solely through verbal lectures and static images. The intrinsic benefit of utilizing computer applications in the learning process is their dynamic response to user input, which provides immediate, visual feedback to students.

Coding-based modules for spectroscopic education of undergraduates have been underscored among the essential tools in the toolbox of an undergraduate chemistry-focused student. Attention has been directed towards this approach, as a number of educational and research articles have been published describing independent or supported programs specifically for the introduction of various spectroscopies to students earlier in their undergraduate careers.[1−4] Though the examples of independent applications provide robustness and a high degree of customizability without sacrificing efficacy, MATLAB serves as an excellent educational platform for educators, with widespread usage and accessibility across a number of universities and industries due to its relatively intuitive syntax and large library of supported functions and programs. A number of examples already exist that employ MATLAB for the specific purpose of spectroscopic education with the focus on introducing a range of topics that are not typical to undergraduate curricula such as time-resolved spectral dynamics, build-your-own spectrum plotting programs, and system modelling and spectral prediction from first-principle equations.[4−6]

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Much of the focus described above, however, has been aimed at developing modules for the display, prediction, and analysis of spectra from infrared and NMR spectroscopies. The wide use of such modules is currently seen as a key link between current chemistry curricula and access to affordable equipment and trained users. However, endeavors have not been extensively focused on a crucial step in the process of spectroscopy: namely, data collection or instrument/equipment operation. Although data acquisition for some spectroscopic techniques such as IR can be presented in such a way that significant user input may not be required for introductory operation, more advanced measurements that can be related to reaction monitoring require spectral parameterization that will allow reproducible data collection with a high signal-to-noise (S/N) ratio in a timely manner. An early decision-making tool that minimizes complexity in spectral acquisition can enable instructors to focus on both the fundamentals and application potentials of the technique while opening new avenues for student development.

The growing presence of Raman spectroscopy in undergraduate education and of course in research in both academia and industry as a whole encompasses a great case study where deeper knowledge is required for accurate and consistent collection using these spectrometers.[7−9] In the case of Raman spectroscopy, intentional and thoughtful operation is at the interface of the true material composition and measured response. Failure to consider the effects or quality of collection, influenced by the operational parameters (microscope objective, gratings, acquisition time, neutral density filters, etc.) decided upon by the user, can result in spectra that are difficult to analyze or even misleading. Therefore, it is of the utmost importance to highlight these considerations as an integral part of user training. While this would be difficult to achieve in a lecture-style setting, an in silico module that exposes new users to this spectroscopic technique in an accessible way by building operational intuition would be highly valuable for the accurate transition to in-person operation.

In a recent report from Parobek et al., the authors present a comprehensive experiment which seeks to introduce upper-level undergraduates to the utilization of Raman spectroscopy in identifying differences in graphene-based materials.[10] From an educational perspective, the authors have made significant efforts in highlighting and discussing the reasons behind the choice of the spectral parameters. However, a usual practice is that this information may be intended to be disseminated verbally to students prior to and during such an experiment to be followed verbatim. Without developing an intuition for proper usage of the spectrometer, such approaches could discourage students when low-quality spectra are acquired for more challenging materials, reacting systems, etc. Providing a concrete, referenceable resource on effective Raman spectrometer operation would assist students in preparing for such lab experiments and troubleshooting potentially unexpected behavior. Software applications are particularly well-suited for this, as students can remotely access the material using a range of devices (computer, phone, tablet), and they do not require each student to have hands-on time with a spectrometer, which would be prohibitive and unrealistic in many institutions considering class sizes and the availability/accessibility of relevant spectrometers to undergraduates.

Towards this end, a MATLAB program utilizing the new App Designer interface was constructed in order to provide students and new users with an interactive interface through which to develop sound intuition regarding Raman spectrometers and their operation. Through this application, students will be potentially able to relate the physical instrumentation of a Raman spectrometer and their selected operational parameters to the resulting spectra of selected materials with similar or different spectral behaviors. This MATLAB application aims on developing a foundational understanding that prepares students for future exposure to Raman spectroscopy, by giving examples of the applications of the technique and accelerating learning curves in their careers, whether it be in industry or academia.

CONSIDERATIONS IN THE ACQUISITION OF RAMAN SPECTRA AT A GLANCE

Although the focus of this contribution is not to delve into the theory regarding vibrational spectroscopies (Raman and IR), the lone fact of the rarity of Stokes scattering, which is the foundation of Raman, relative to Rayleigh elastic scattering, accounts for the challenges that are associated with large operational discrepancies between Raman and IR. This relative rarity requires that lasers with power greater than 10 mW are utilized in any system in order to ensure that a sufficient Stokes signal is generated such that it can be detected.[11] Though more signal is almost always beneficial in reducing the deleterious effects of instrumental noise in the data, there is a balancing act that must be managed by the operator that seeks the optimal S/N that (i) does not overheat the material of interest while being collected and (ii) ensures timely collection without sacrificing spectral information acquired. A characteristic example of such overheating is shown in Figure 1 for

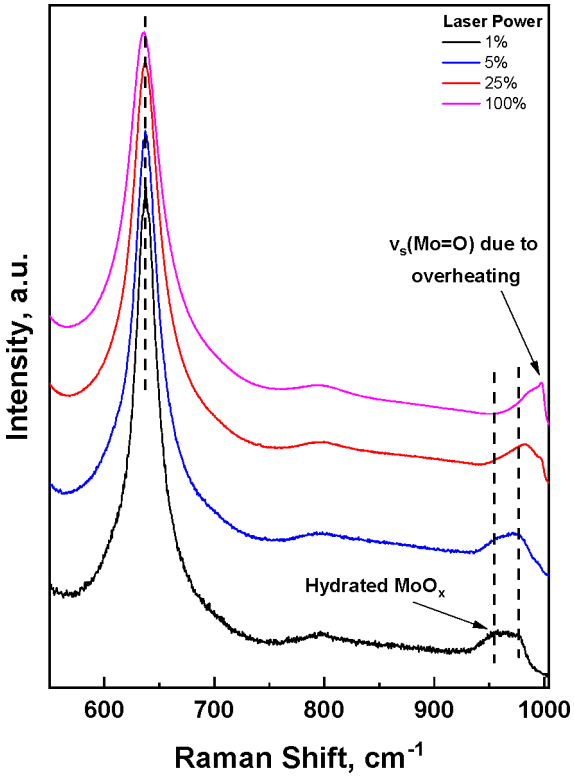

Figure 1. Example of how laser intensity (adjusted by neutral density filter) affects the information acquired for MoO_3/P25 catalysts when spectra are collected at identical conditions.

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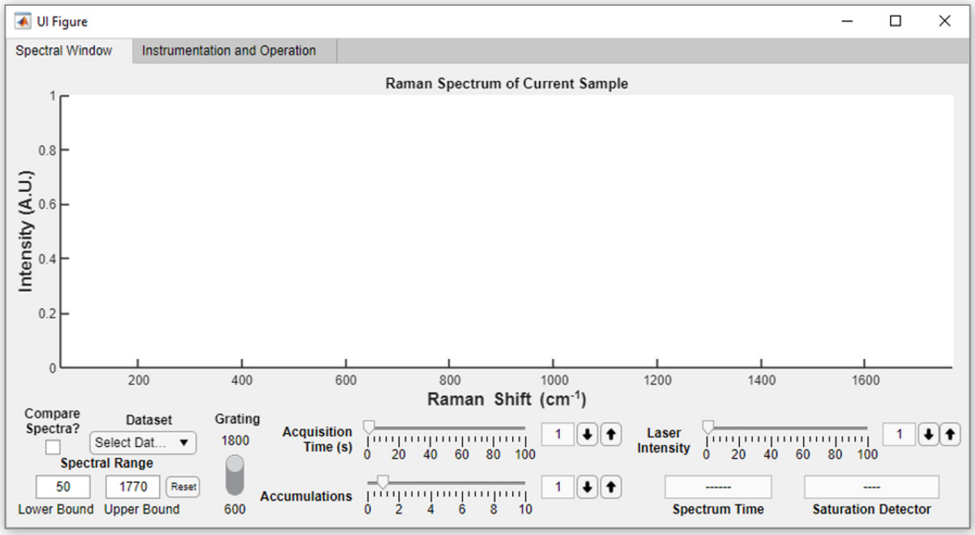

Figure 2. Graphical user interface (GUI) shown at application start-up. This provides access to interact with various spectroscopic parameters with real-time plot updates.

MoO_3/TiO_2 catalysts. Under ambient conditions, it is well-recognized that MoO_x dispersed species are highly hydrated, and thus, a broad band around 950−975 cm^{-1} is expected.[12−16] As shown in Figure 1, although an overall improved S/N is observed, it is clear that, for fixed spectral parameters, there is an evolution of the spectra obtained upon changing the neutral density filter used, i.e., the laser power that the sample senses, that is associated with the gradual dehydration of the catalyst surface. This simple example underscores the importance of connecting spectral acquisition parameters with the real state of samples studied to avoid misinterpretation of structural implications. Therefore, it is crucial that the operators have the proper experience to note when these changes may be occurring in their system and that they have the knowledge to react and modify the spectral collection accordingly in order to mitigate these effects.

In recent years, Raman spectra have been acquired using a microscope, and thus, hands-on training with these techniques is required to select an optimal combination of laser line and microscope objective. However, the quality, as well as time of the Raman spectra collected, depends strongly on a large set of parameters such as choice of gratings, acquisition time, number of accumulations, neutral density filters, and aperture. These parameters need to be selected simultaneously, and perturbing one of them even slightly can significantly impact both S/N and total collection time. Besides these parameters, it is of utmost importance here to mention that the choice of the excitation source is critical. For instance, by employing a lower-energy laser source, such as 785 nm, the user can mitigate any fluorescence effects that usually obscure any vibrational features when visible sources (e.g. 532 nm) are used. In addition, the choice of laser source can be of paramount importance when the resonance Raman effect is considered. Regardless of whether the experience is in-person or virtual, the most important aspect of Raman spectroscopy education is that an understanding is developed regarding the synergistic relationship between operation and instrumentation. Next, we introduce a MATLAB application that can serve as the interface between online and in-person training/education in Raman spectroscopy.

MATLAB APPLICATION AND RELEVANT EXAMPLE

A MATLAB GUI was written with the goal of fostering autonomy and intuition regarding the operation and collection of representative, publication-quality Raman spectra. As this GUI was written with the App Designer program introduced to MATLAB with Release 2016a, the program is accessible via the download of a compiled single-file application through the link included with the Supporting Information. The benefit of this distribution, particularly over the older MATLAB GUIDE program, is the ease of operation through a single executable if the user can access a licensed MATLAB program and the possibility of using a web application even without a MATLAB license. This removes a significant barrier in student usage by avoiding the necessity of a license to MATLAB, although access to the base program code for independent modification still requires a license at this time.

The primary functionality of the program involves a plot window (Figure 2) that displays a selected material's Raman spectrum (from dataset), collected using the interactive user parameters that are available below the plot window. These user parameters, namely, acquisition time, accumulations, laser intensity, and grating resolution, are crucial parameters for the operation of Raman spectrometers, with a significant influence on the resulting spectral quality. However, in many experiments paired with Raman spectroscopy, these settings are either provided by the instructor or not discussed, meaning that students are not able to develop an intuitive sense of their physical attributes, hampering their independent usage in future situations, whether in academia or industry. In the use of this application, students will be free to change these parameters (in the range reported in Table 1) and have the resulting spectrum displayed instantaneously. This immediate feedback to incremental changes in the settings has the potential to reinforce the students' understanding of the relationship between collection and common spectral problems such as noise, low intensity, and resolution. Apart from the spectral results that are correlated with the collection parameters, the estimated time of collection is also reported, as this is an important, yet often overlooked, consideration when collecting spectra. The spectral quality, in general, should be

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Table 1. Spectral Parameters and Range of Relevant Changes Considered

Parameter	Range
Acquisition time	0−100 s
Number of accumulations	0−100
Grating	600 or 1800 gr/mm^2
Neutral density filter	1−100%

optimized with respect to the minimal collection time needed. In this way, laser source life spans are maximized, and the deleterious effects of local laser heating are also reduced, though this may still play a role if laser power output is too high.

It is important to notice here that the response of each material under fixed spectral parameters varies significantly with the intrinsic properties of the material such as the composition and Raman cross section of individual components that aimed to be measured. Towards this end, the initial version of this application is paired with a set of spectra that embody the full range of behavior that a student might expect from any given material in the future. As a case material, we have focused on MoO_3/P25, an important material in the field of heterogeneous catalysis,[17,18] where Raman spectroscopy has been a powerful tool to fully unravel the molecular structural changes occurring on the surface under varied environment conditions. A characteristic example is shown in Figure 3, where the same material, i.e., MoO_3/P25, is evaluated at different spectral parameters with the intention to maximize the S/N ratio. Besides their importance in the field of catalysis, these supported materials make excellent case studies of the obstacles usually faced in Raman spectroscopy due to the variations in their intrinsic Raman scattering behavior (cross section) of the support and/or active phase, as well as the low concentration of the supported species. Focusing on acquiring high-resolution spectra of the dispersed phase might lead to saturation of the detector in the vibrational regime where the main crystalline phase can be detected. Thus, care must be taken in collection in order to return a spectrum that reduces noise and increases signal sufficiently to separate the two components and allow for analysis of the surface species. In the current version of the application, users also have the capability to intervene and upload their own set of spectral data by employing a simple upload feature, described in detail in the Supporting Information. This feature allows the instructor to create a larger subset of different materials (solid, liquid, gas) that can serve as a better learning activity while at the same time allows advanced users (e.g., lab PIs, industrial personnel, etc.) to develop a complete training set.

FUNCTIONALITY, ADAPTABILITY, AND FUTURE LEARNING OPPORTUNITIES

While this application can, and should, be used as an independent learning opportunity to grasp the techniques that lead to the collection of quality Raman spectra, there exist numerous opportunities for students to engage in active learning projects in MATLAB and Raman spectroscopy, where available. The app itself is a collection of the basic tools and functions needed to display the intended Raman spectrum in a manner that is easy to use and clearly conveys all of the necessary information. The app itself is a collection of the basic tools and functions needed to display the intended Raman spectrum in a manner that is easy to use and clearly conveys all

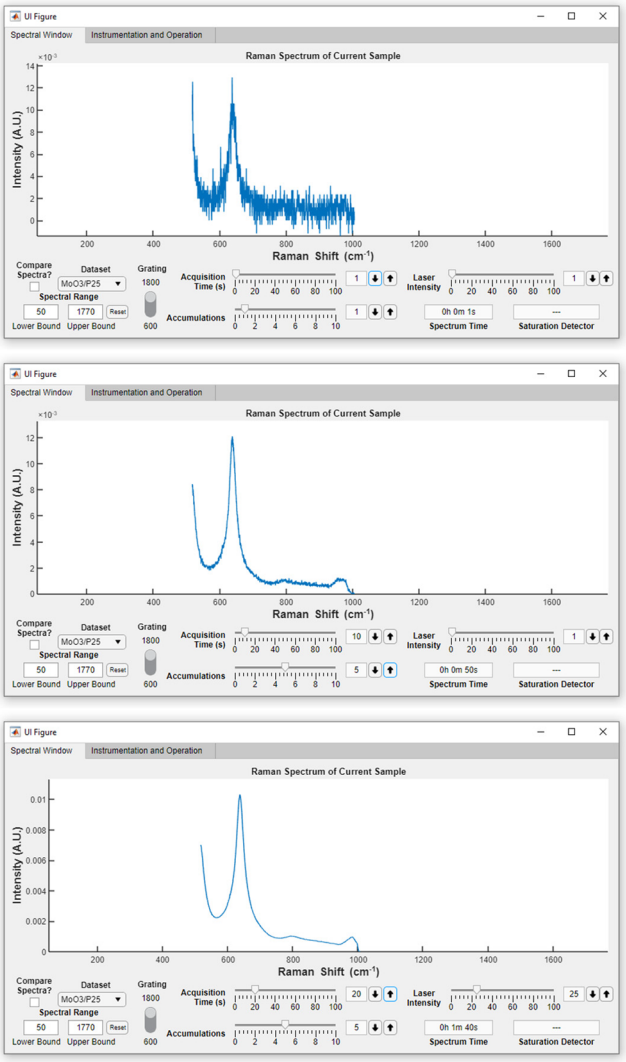

Figure 3. Visualizing spectral quality and total spectral time while changing various parameters via the in silico interface.

of the necessary information. We suggest that this app can complement lectures in the context of courses that are relevant to instrumental analysis and/or molecular spectroscopy; a suggested demonstration with relevant learning outcomes for undergraduate students is presented in the Supporting Information. In addition, the app can be used as a tool for preparing junior/senior students to acquire fast kinetics via Raman spectroscopy potentially in the context of process engineering labs. A worthwhile project for students might be to build a similar app from scratch, or to add functionality to the existing app by using the already built code as a scaffold and example upon which to build, depending on the coding experience of the students. Although such a project would, in principle, require a very specialized background for undergraduate students (e.g., chemistry and computer science majors), the user friendly environment of the App Designer can extend its use to disciplines where coding/programming skills are not thoroughly discussed. However, such an implementation can boost student motivation and learning abilities to fields that are not typical for traditional undergraduate curricula.

The App Designer environment in MATLAB in which this application was built is highly intuitive, utilizing a dot notation

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to identify variables and functions within the app. Though this is largely different from the syntax of independent scripts in MATLAB, it is relatively easy to adapt the notation after being presented with an example. The addition of interactive buttons is done largely visually, by clicking and dragging objects from a preloaded MATLAB library. Functionality is then added to these objects in a separate coding window, which provides line-by-line debugging information should issues arise in the application operation.

Whether the task is to design an app from scratch or to simply modify the existing framework, a secondary lesson apart from the coding experience is the presentation of scientific information to the community at large. Communication in the scientific fields is of the utmost importance, and the design of an application interface that is both easy to use and informative is at the center of this project. Once the students have developed an understanding of the basics of Raman spectroscopy and the fundamental operation of these spectrometers, it is up to them to decide which inputs are relevant, which inputs are not, and how these should be displayed in a manner that makes interaction with the application easiest. The current version of this application provides an opportunity for teaching as well as training purposes. It is important here to mention that future endeavors should also be placed on acquiring a large set of learning outcome data from undergraduate and graduate students in different disciplines. This set of data should be used as a feedback loop for continuing improvement of the application. Learning outcomes can be acquired either by implementing short quizzes after the demonstration of the application (in the case that students/instructor do not have access to the required instrumentation) or via hands-on exposure in the context of any instrumental analysis or spectroscopy course.

In schools with undergraduate access to a Raman spectrometer, other modifications to the program become possible as well. Students could be tasked with adding another element into the preloaded library (e.g., size of the aperture, distance from best focus, etc.) after collection of the spectra in a hands-on class assignment. In this way, students interface with the Raman spectrometer directly, gain insight into an additional element's Raman response characteristics, and must interface with the application syntax in order to seamlessly add the new element to a drop-down list (or buttons) and plot the data accordingly. As this would include the collection of raw data from a spectrometer, discussions might include the analysis of spectroscopic data, particularly regarding normalization, spectral time, and S/N and the proper methods to obtain accurate data without modification.

Beyond the education of undergraduate chemistry students, it is also possible that this application might serve as an initial step towards further exploration into methods for teaching a proper spectroscopic collection technique, particularly regarding Raman. It is not outside of the realm of current capabilities for one to imagine and develop a machine learning application in a similar vein, which collects mass quantities of Raman spectra and calculates a "quantitative" signal-to-noise ratio, rather than relying on the qualitative human approach as shown here. In addition, one may be able to link the experimentally derived data shown in this application with theoretically calculated spectra where the specific vibrational modes can be also visualized. Such a program would enable the computational prediction or suggestion of proper spectroscopic parameters given a desired signal-to-noise ratio or material specification as selected by the user. In the examples provided within the application here, the signal-to-noise ratio must be high enough to conclusively detect and analyze surface species at relatively low concentrations. This optimal signal-to-noise ratio could presumably be arrived at by considering the relative concentrations of the vibrational species being studied as well as their respective Raman cross sections. Such an endeavor is outside of the scope of this report but would surely be an invaluable tool both in the educational sector as well as throughout academia and industry, as a robust machine learning algorithm might be expected to surpass even experienced users.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c00925.

Instructions and relevant features of the application (PDF, DOCX)

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Notes

The authors declare no competing financial interest.
The application is available at https://www.gtsilomelekis.com/downloads.

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