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Low-Cost, Balle-Flygare-Type Cavity Fourier Transform Microwave Spectrometer and Pure Rotational Spectroscopy Laboratory for Teaching Physical Chemistry and Astronomy

Amanda Duerden, Nicole Moon, and G. S. Grubbs, II*

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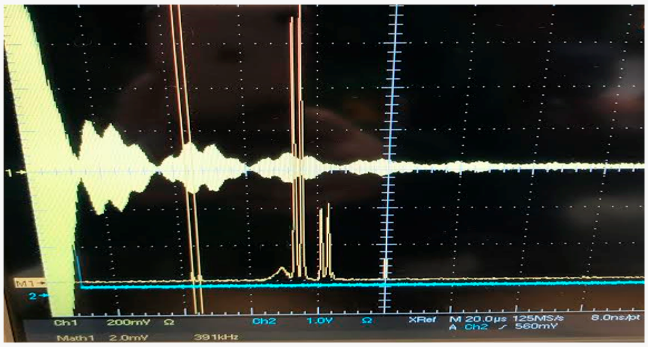

ABSTRACT: Few laboratory exercises exist that introduce undergraduate students to both the concepts and instrumentation used in rotational spectroscopy. Because of this gap in undergraduate laboratory training, a teaching laboratory for the pure rotational spectroscopy of benzonitrile has been developed and reported. Owing to benzonitrile's recent discovery in space, the molecular spectroscopic technique and target are applicable to both the physical chemistry and astronomy disciplines. Because of the size of the dipole moment and relative safety of the molecule chosen, the laboratory approach allows undergraduates to directly load, tune, measure, and assign spectra using the same quantum chemical approaches and spectroscopic assigning tools available to a researcher in the field. Concepts taught in this laboratory include the rigid and semirigid rotor, as well as low-level nuclear electric quadrupole coupling Hamiltonians. To minimize the budget and allow the students to get hands-on training with the rotational spectroscopy instrumentation, an interactive, low-cost, Balle-Flygare-type, cavity Fourier transform microwave (FTMW) spectrometer of research-grade quality was developed and is reported. Implementation of the laboratory exercise, time of exercise, and student response to the exercise is also reported.

KEYWORDS: *Upper-Division Undergraduate, Physical Chemistry, Hands-On Learning/Manipulatives, Spectroscopy*

■ INTRODUCTION

Pure rotational spectroscopy has traditionally been used as a tool in the determination of gas-phase molecular structure inclusive of bonding strength,[1,2] geometry,[3,4] conformation,[5] and internal rotation barriers.[6] Recently, rotational spectroscopy techniques even demonstrated the capability to qualitatively and quantitatively determine chiral species in chemical mixtures.[7,8] Considerable amounts of information can be garnered from a rotational spectrum, benefiting a wide variety of areas including, but not limited to, atmospheric chemistry,[9] synthetic processes,[10] astrophysics/astrochemistry,[11] pharmaceuticals,[12] and instrument development.[13,14]

Despite the growing use of rotational spectroscopy as a modern-day physical/analytical chemistry tool, students at the undergraduate level are rarely introduced to the theory, research, or instrumentation present within this field. While a variety of plausible explanations exist, one compelling reason for this continued omission is that many textbooks do not cover the experimental aspects of the spectroscopy or marginalize its use. As new techniques and implementations of the technique are found for rotational spectroscopy, students will need education and experience with these methodologies. Another reason students may lack exposure is that the theory involved is inclusive of high-level mathematics and usually not introduced to an undergraduate until close to the end of their career (if at all). In other complex theoretical chemical spectroscopic techniques such as FTIR and NMR, spectra are usually introduced to undergraduate students via pattern recognition techniques well before any theory is taught.[15] In this way, students build familiarity with these spectra while still being able to draw useful spectroscopic insights. Cooke and Ohring[16] recently presented a similar approach for rotational spectroscopy whereby students use patterns to identify types of spectra. Simple algebraic relationships are shown to govern the appearance of the spectra, which minimizes a student's required math level in order to assign quantum numbers to a spectrum.

Despite these tools, however, the only hands-on experience with rotational spectroscopy usually available to undergraduates is to join a microwave or millimeter-wave spectros-

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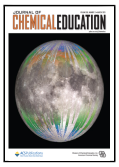

copy research laboratory, as most of today's research laboratories exist in academic settings. This is not an option for undergraduate students whose universities do not have access to such a research lab. As a result, most undergraduate students are unable to gain hands-on experience within the field.

Two major obstacles must be addressed to facilitate educating students and providing an opportunity for hands-on experience with microwave rotational spectroscopy. The shortage of quality laboratory exercises on the subject, and the cost of the instrumentation. Currently, two of the most commonly used microwave rotational techniques are a Balle-Flygare-type, cavity Fourier transform microwave (FTMW) spectrometer[13] and a chirped pulse, Fourier transform microwave (CP-FTMW) spectrometer.[14] The FTMW spectrometer is a narrowband (~1 MHz) technique while the CP-FTMW is a broadband (typically 1−12 GHz) approach. Although there are companies who sell microwave spectrometers, both approaches are generally not commercially available and are custom built by research laboratories to address a specific research agenda. As a result, research laboratories using these techniques in the teaching mission bare both the cost of the parts needed to build the instrument and the person-hours needed to construct and maintain it. Research-worthy instruments, on the low-end, can cost upward of $150,000 for the circuit design, sourcing, and vacuum system. This cost, along with the needed expertise, typically prohibits all nonresearch universities from having such an instrument for undergraduate student use. Even when a university possesses a microwave rotational instrument, students may still be unable to gain hands-on experience, possibly due to a lack of available laboratory exercises or the reluctance concerning students interacting with the instrument to protect it from damage. The few microwave spectroscopy laboratory exercises that are available for use within the undergraduate physical chemistry laboratory are either outdated for current microwave spectroscopy tools,[17,18] are not the same instrument tools used as the researcher,[19−23] cost prohibitive,[20] or are computational paper laboratories that simulate results acquired by rotational spectroscopy. Consequently, students gain little or no practical skills within the field and are often left confused as to how to apply this subject matter to any potential physical and/or chemical investigations.

In response to this, a physical chemistry laboratory for the acquisition and analysis of the pure rotational spectrum of benzonitrile is presented. Benzonitrile is a relatively safe, stable, inexpensive chemical that is also of astrochemical/astrophysical interest due to its recent discovery in space by similar rotational spectroscopy/radioastronomy methods.[11] The laboratory has been designed around a reduced-cost, research-grade Balle-Flygare FTMW instrument that can conceivably be built with inexpensive second-hand circuitry, vacuum chambers, and components commonly found in storage spaces of chemistry and physics departments. Within the laboratory design, students have the opportunity to (i) make quantum chemical calculations using Gaussian 09 software,[24] (ii) get direct, hands-on experience operating the spectrometer for the collection of spectra, and (iii) analyze data they have collected with free software tools commonly available to the spectroscopic community. Along with hands-on opportunities, the desired outcomes of this experiential learning exercise are that students become more familiar with the quantum theory of rotational spectroscopy, angular momenta coupling, and the interplay between theoretical and experimental approaches. The design and execution of the lab will be discussed.

PHYSICAL CHEMISTRY ROTATIONAL SPECTROSCOPY LABORATORY OVERVIEW

A copy of the physical chemistry laboratory handout used can be found in the Supporting Information. In addition, this teaching laboratory was presented at the 74th International Symposium on Molecular Spectroscopy (ISMS) where additional slides can be found and accessed.[25] The laboratory course in which this lab is performed is one semester long; each period consists of 1 h of recitation and 4 h of experiment time. The baseline material needed to perform this lab is covered in the recitation while the conceptual material is left to a required course in Quantum Chemistry. We are able to have two groups of students perform this experiment during one laboratory period and the students are given 2 weeks to analyze, write up, and submit a laboratory report. The course, entitled Accelerated Physical Chemistry Lab, includes eight other experiments in order to cover a breadth of topics in physical chemistry with this lab being number seven in the sequence. The laboratories, with topical areas in parentheses, are

1. Bomb Calorimetry (Thermodynamics and Uncertainty Calculations)
2. Vapor Pressure using the Clausius−Clapeyron Equation (Thermodynamics)
3. Differential Scanning Calorimetry (Thermodynamics)
4. Brownian Motion and Statistical Mechanics (Experimental Derivation of Boltzmann Constant)
5. Nuclear Magnetic Resonance and Kinetics (Kinetics)
6. Conjugated Molecule Absorption Spectra/Particle-in-a-Box (Quantum Mechanics)
7. Microwave Spectroscopy of Benzonitrile (Quantum Mechanics/Spectroscopy)
8. HCl/DCl Rovibrational Spectrum (Quantum Mechanics/Spectroscopy)
9. Electronic Spectrum of I_2 (Quantum Mechanics/Spectroscopy).

In five of the nine exercises (laboratories 1, 6, 7, 8, and 9), students perform quantum chemical calculations, so they are very familiar with how to run such calculations by the end of the course. Furthermore, students are asked to manually assign rovibrational and electronic spectra in both the HCl/DCl and I_2 laboratories and utilize linear least-squares regression tools in Microsoft Excel in order to fit these data to an appropriate Hamiltonian. This gives them insight into the genesis and methodology of quantum number assignments and recreates, in a less intimidating fashion, the mechanism of quantum chemical Hamiltonian tools.

From a teaching lab standpoint, there are three (3) goals or objectives of this laboratory exercise: (i) set up and successfully execute a geometry optimization at the B3LYP/6-311G++(d,p) level for benzonitrile using Gaussian 09 software; (ii) interact directly with and acquire spectra on a research grade FTMW instrument; and (iii) perform effective Hamiltonian fits inclusive of nuclear electric quadrupole coupling using analysis software commonly available to the spectroscopic community (Pickett's SPFIT/SPCAT software).[26] The students perform (iii) during the two-week analysis and writeup phase and, although guided by the laboratory handout, are encouraged to get help from the instructor or teaching assistants as this software can be challenging. Through these three exercises, students experience for themselves the process microwave spectroscopists use to predict and analyze spectra while gaining hands-on instrument experience. It is understood, however, that performing the experiment in its entirety could pose problems with other laboratory timeframes. In these situations, it is suggested to only perform one of two subsets of the laboratory experiment: (1) quantum chemical calculations and acquisition of spectra in order to show agreement of experiment with quantum chemical calculations or (2) acquisition of spectra with subsequent fitting using Pickett's SPFIT/SPCAT program suite. Either option provides unique insight into rotational spectroscopy while maintaining the instrumental aspect of the laboratory exercise.

To execute this process, students must familiarize themselves with the theory and concepts present within rotational spectroscopy such as rigid rotors, angular momentum operators, selection rules, and quadrupole coupling.[3,4] The students taking this course are required to have either taken a formal quantum chemistry course or be concurrently enrolled. While this alleviates some of the formal presentation of rotational spectroscopy knowledge, baseline material needed in these areas for the laboratory exercise are introduced during the 50 min recitation section. One area of concern, however, is that the genesis of asymmetric top quantum numbers is not discussed in either the course or the lab, nor are the hyperfine coupling quanta, F, arising from nuclear quadrupole coupling. However, the equations governing these elements are discussed in the laboratory handout and recitation (see Supporting Information). During the recitation, the effects of these elements are discussed from a classical point-of-view by showing the students that there is need for more quantum mechanical descriptors as masses are more asymmetrically distributed in the principal axis system. Furthermore, it is explained that if the masses themselves are not evenly distributed (have asymmetry due to spin), we must also account for that with another quantum mechanical descriptor. From there, a pattern recognition approach for types of spectra arising from the dipole moment components and selection rules using the paper by Ohring and Cooke[16] is used for changes in quantum numbers. Admittedly this can be described as a hand-wavy approach, but the purpose of this laboratory exercise is to familiarize students with what rotational spectroscopy is measuring and how it is measured; much like what is done when students first see and interpret NMR and FTIR spectra.

During the development of the laboratory exercise, the first decision to make was the molecular target. For a molecule to be considered, it had to produce a strong molecular signal (be volatile and possess a strong dipole moment), be inexpensive to purchase, relatively safe for students to handle, and have some link to the broader scientific community. The last requirement was made to demonstrate to the students in what situations rotational spectroscopy may be implemented while also showing them that the field is a very vibrant, active, and important area of molecular spectroscopy. Because most students are captivated by astronomy and rotational spectroscopy is the basis for identifying many molecules in space, it was decided that astronomy be this link. To simplify the experiment, the molecule should also not possess multiple conformations, spin−spin, or spin-rotation interactions that could complicate the analysis and prevent novice students from being able to successfully complete a spectral fitting assignment in a timely manner. From these requirements, it was ultimately decided that benzonitrile was the molecule of choice as it meets all requirements and was recently discovered in the interstellar medium.[11] For the laboratory, ≥99% pure benzonitrile was acquired from Sigma-Aldrich and used directly.

Although traditional rotational spectroscopy research would not follow this path, in the interest of time, acquiring spectra is done first. Traditional rotational research would start with a prediction and then follow with a search for transitions in a region where transitions are predicted. While this was followed in spirit, approximate transition positions of benzonitrile were predicted by using the provided rotational spectroscopic parameters in ref 27 in Pickett's SPCAT software. A listing of frequencies near the transitions is presented in Table 1. The frequency range for this listing is 8 to 12 GHz because it provided an abundance of transitions for measurement and it required no interchange of microwave electronics, saving lab time. From this range, 21 transitions within 16 separate tuning frequencies—containing a wide range of strong and weak transitions—were selected for observation. During the development stage, it was discovered that 21 transitions were ideal as they provided students with enough data to produce a Hamiltonian fit while also allowing the laboratory to easily be conducted by two groups independently within one scheduled class period (4 h total, or 2 h for each group). Because of the coaxial orientation of the nozzle, transitions appear as Doppler doublets.[28−30] For each transition measurement event, students set up the instrument, tune to the desired frequency, collect the spectra, and calculate the line center for each observed doublet. Details regarding instrument design and operation can be found in the Low-Cost Balle-Flygare Instrument Design and Operation section.

Table 1. Tuning Frequencies for the Experiment

Frequency/MHz			
8205.4	8359.8	10343.8	11082.0
8206.6	8361.2	10344.8	11085.0
8282.8	8361.9	11030.3	11219.4
8284.1	8769.8	11080.8	11220.0

To achieve all objectives while also staying as close to a true rotational research experience as possible, students are also tasked with performing quantum chemical calculations using Gaussian 09 software made on the university's high-performance computing cluster. These quantum chemical calculations include rotational and nuclear electric quadrupole coupling constants in order arrive at preliminary values for the construction of an effective Hamiltonian fit of the system. The calculation performed is a geometry optimization at the B3LYP/6-311G++(d,p) level with the keyword output=pickett in order to get a direct input file for the SPFIT/SPCAT program suite. Gaussian 09 was chosen simply because Missouri S&T has a site license and students have access to the front-end, GaussView 5.0, allowing them to easily create input files for the program. Once the calculations were complete, students imported the findings of the calculations into Pickett's SPCAT/SPFIT programs suite[26] to analyze the spectra they collected and develop a proper effective Hamiltonian for their molecular assignment. Although helpful, access to Gaussian software is not required. However, students will need predictions for the rotational constants and diagonal

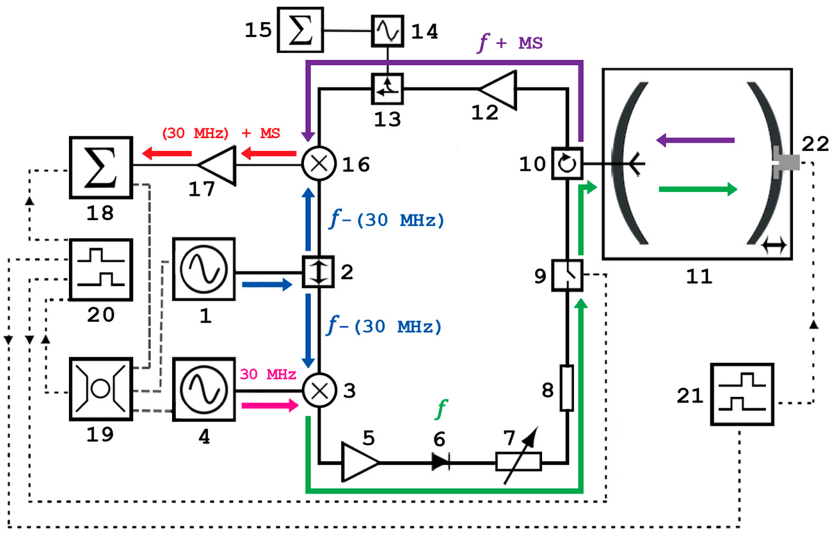

Figure 1. Circuit diagram for the 7.5−18 GHz Balle-Flygare type, cavity FTMW experiment at Missouri S&T in detection mode. The instrument design detects on the heterodyne of a 30 MHz signal. See text for the creation and detection of signal. The components are listed as follows: (1) Anritsu MG3693B microwave synthesizer (up to 30 GHz); (2) Midwest Microwave MFR 34078 PWD-5526-02-SMA-79 power divider (6−18 GHz); (3) Miteq SME0618LI1A single sideband mixer (6−18 GHz); (4) HP 8340A microwave synthesizer (10 MHz-26.5 GHz); (5) Microsemi L0818−30 power amplifier (1 W, 8−18 GHz); (6) DITOM DMI6018 isolator; (7) Radiall Dot MICRONDER (9) General Microwave F9114 single pole, single throw PIN diode microwave switch (1−18 GHz); (10) Miacom ML3G-9700 (7.5−12.4); (11) Fabry−Perot cavity resonator with SMA cable coupling antenna and supersonic pulse valve inside vacuum chamber; (12) Miteq JS3-08001200-12-10P (8−12 GHz), Miteq JS4-12001800-16 (12−18 GHz), Miteq AFS4-02000800-09-10P-4 (2−8 GHz) low noise amplifier; (13) Narda 4203-16 directional coupler (2−18 GHz, 16 dB secondary output); (14) Wiltron 75KC50 crystal detector (10 MHz−40 GHz); (15) Tektronix TDS1002 oscilloscope (60 MHz, 1 GS/s); (16) Miteq IR0218LC1A image rejection mixer (2−18 GHz); (17) RTI RTPA-5-3010 RF amplifier (30 MHz, 10 MHz Bandwidth, 30 dB Gain, 2.5 dB Noise); (18) Tektronix TDS5054B oscilloscope (500 MHz, 5 GS/s); (19) Standford Research Systems 10 MHz reference with distribution amplifier and PPS source; (20) Quantum Composers 9528 pulse generator; (21) timing control and power supply driver (homemade) for Parker-Hannifin Series 9 solenoid valve; (22) Parker-Hannifin Series 9 solenoid valve with 0.5 and 0.8 mm flange.

nuclear quadrupole constants (χ_{aa}, χ_{bb}, and χ_{cc}) from an optimized structure in order to generate accurate transition predictions in SPCAT. Since benzonitrile is planar and does not possess any conformational freedom, only one modest, fast method and basis set is required for an adequate set of constants. Furthermore, the nuclear quadrupole coupling constants just need to be close (within 10 MHz) to their actual values as small deviations do not noticeably change the look of the spectrum.

The entire laboratory writeup, which includes a discussion of the rotational constants, centrifugal distortion parameters, nuclear electric quadrupole coupling constants, and general rotational selection rules, is found in the Supporting Information. Nuclear electric quadrupole coupling is only briefly discussed so students can recognize its effects on the spectra and origin of quantum number, without unnecessarily confusing them given its somewhat complex nature. However, students are asked to explain what a nuclear electric quadrupole constant may probe with regards to bonding. To answer this question, they are asked to consult the literature by Townes and Dailey[31] as well as Novick.[32]

■ LOW-COST BALLE-FLYGARE INSTRUMENT DESIGN AND OPERATION

For students to have chemical training on research-grade instrumentation, they must have access to such resources. This can be very difficult because physical chemistry equipment can be very expensive. The backbone items of a modern physical chemistry research laboratory—spectrometers, calorimeters, lasers, etc.—can easily cost \$100k or more. If instructors possess a few of these items, and are not reluctant for undergraduates to use them, there are texts that are good teaching lab resources.[33] For microwave spectroscopy in particular, research instrumentation access is rare as instruments are commonly home-built. The two most common instrument designs, mentioned earlier, are the narrowband FTMW[13] and the broadband CP-FTMW.[14] The narrowband instrument is a cavity design utilizing a Fourier transform and is often abbreviated FTMW to highlight this. The broadband CP-FTMW instrument has a free space design. The Fourier transform used in both generates a spectrum in the frequency domain from the time-domain collected data. The time domain data are in the form of free induction decays (FIDs), and the governing equations are the Bloch equations making these techniques, in many ways, the electric analogues of the nuclear magnetic resonance (NMR) experiment.[13,14,34−36]

Both instruments, however, are usually very expensive for a common undergraduate teaching lab with the less expensive being the FTMW experiment at approximately \$150k. The CP-FTWM experiment, however, greatly varies due to its range of designs (from approximately \$75k to > \$1 million), but a reasonable, approximate average price is \$250k. One advantage of working with microwave and radiowave electronics is that components are continuously getting smaller, more powerful, and less expensive with each passing year. Understanding where to spend money and the careful selection of components allows for the construction of an inexpensive, yet still research grade instrument; especially in the cases of a department or college already possessing certain equipment on hand. As it is inevitable that some components will need to be purchased, and radiowave electronics are

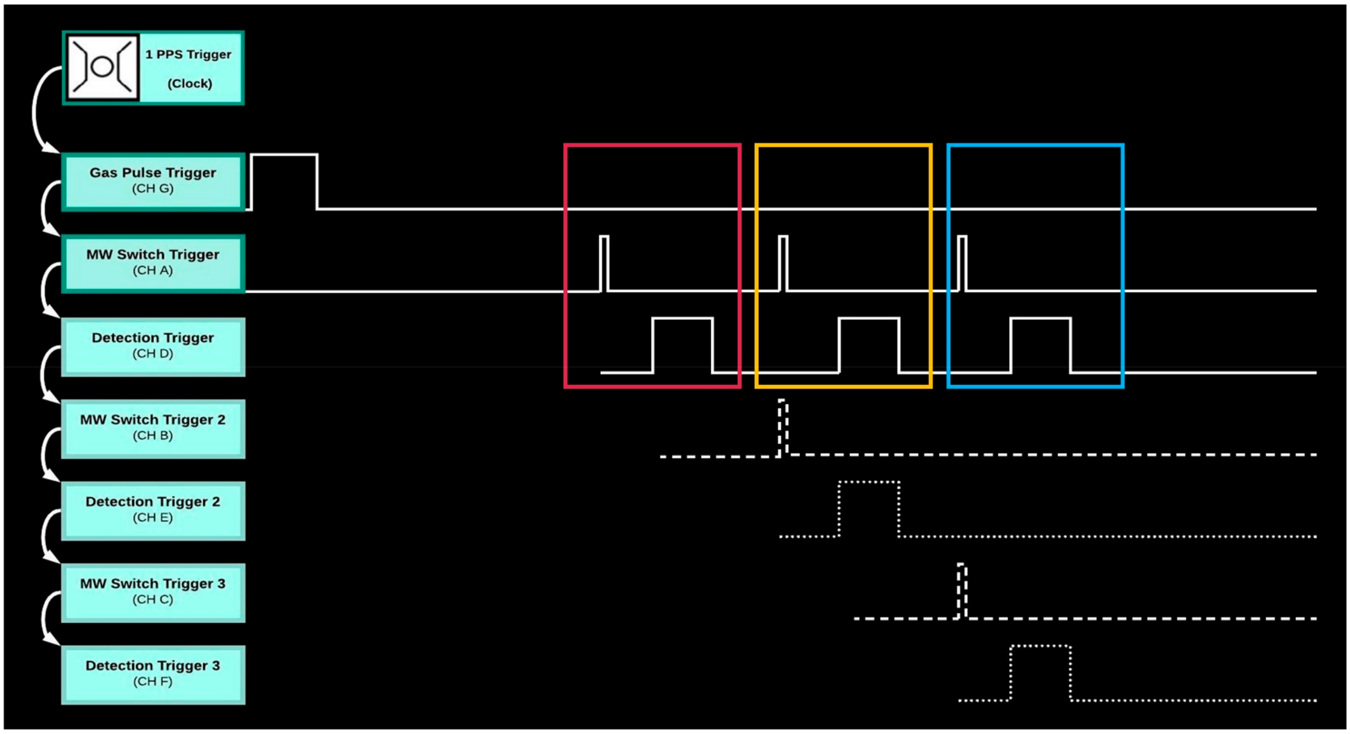

Figure 2. Not-to-scale schematic of the triggering sequence for the FTMW experiment. The channels are multiplexed to generate 3 FIDs per gas pulse. Each excitation/detection scheme is enveloped in a color in the diagram. The first excitation/detection is enveloped with red, the second with yellow, and the third with blue.

typically much less expensive than their microwave equivalent, the FTMW technique is (generally) the better option for keeping costs low. This is because signal manipulation and interpretation is typically performed on the heterodyne of the transition frequency in this technique, allowing much more freedom to utilize radiowave circuit components.[13,28,29]

A schematic for the Balle-Flygare instrument at Missouri S&T can be found in Figure 1. The original intention was for this instrument to be used in both the research and teaching missions, but the bulk of its use has been teaching, and we have found that the rugged nature of the instrument circuit design allows for shutdown with only a 1−2 day start-up preparation period before the lab is performed to check for any problems. As constructed, this instrument can be built for approximately \$50k. The bulk of this cost is the vacuum chamber, cavity, and vacuum system which are very difficult costs to lower. However, this work will focus on showing how the circuit can be constructed in order to minimize an overall instrument cost in the event that a teaching mission has some parts on-hand. Very intricate details of the experiment such as mirror design for maximum molecular interaction, microwave coupling to the experiment, and the mathematical theory is outside the scope of this work, but can be found in refs 13, 28−30, and 34 with direct information about this instrument design being found in refs 37−39. The instrument can be broken into three main sections: (i) excitation (green in Figure 1), (ii) molecule−radiation interaction and response (purple in Figure 1), and (iii) detection and interpretation (red in Figure 1). Furthermore, there are two modes of operation for the instrument: (i) cavity tuning and (ii) data collection. We have provided the finer details of construction and operation, as well as some tips, in the Supporting Information. The instrument was presented at the 74th ISMS where additional content can be found and accessed.[37] A brief overview of the instrument, however, is provided below.

Before the experiment takes place, the benzonitrile sample is loaded into a sample line forming a “U”-shape in the tubing. Industrial grade argon is used to pressurize the line to approximately 2−3 atm absolute pressure (this will vary, but best signals tend to be in this range) so that the argon bubbles through the sample, but the sample does not escape the “U” in the tube. The instrument is tuned to a mode for a frequency near (<0.5 MHz away) a transition frequency as described in the Supporting Information. The mode tuning frequencies are presented in Table 1 as well as in the Supporting Information. After tuning, the instrument is ready for operation.

The experiment begins with a pulse of the gas into a vacuum chamber held at 5×10^{-6} Torr. The gas pulse is achieved using a Parker Series 9 solenoid valve with 0.8 mm orifice. This is controlled by a homemade valve control box which is triggered by a square wave from a Quantum Composers 9528 delay generator. The experiment triggers are shown in Figure 2 (not to scale). The initial trigger of the delay generator is governed by a pulse per second (PPS) signal from a Stanford Research Systems 10 MHz, Rb clock to ensure timing stability. All other time-sensitive items such as the microwave generator and oscilloscope use the 10 MHz as an external reference signal. The homemade valve control box controls the width of the pulse, usually about 300−500 μs, which is dependent on the diffusion pump speed and pulse frequency of the nozzle (i.e., 5 Hz is 5 nozzle pulses per second). For our experiment, the pulse frequency of the nozzle is 1 Hz. The sample introduction method creates a supersonic expansion molecular beam that cools the sample rotationally to ∼1 K.[13] This aspect of the experiment is not covered in the delivery of the lab, but could provide a teaching tool for statistical thermodynamics. We use it because the cold rotational temperatures give favorable populations to the lower rotational states, making the spectra simpler and more intense in the operational frequency range of the spectrometer.

After the gas pulse, the molecules in the chamber interact with the light. Because the molecular relaxation is on a time scale much faster than that of the evacuation of the molecules (microseconds versus many milliseconds, respectively), we can use multiple microwave pulses per gas pulse to gain more signal out of each sampling event. The successive events are not as strong in intensity as the first microwave pulse, but the signal-to-noise advantage is significant, resulting in extreme time savings because the signals are coadded.[14,40,41] There are two aspects of a microwave pulse that must be controllable, the delay—when to trigger the microwaves (variable, but usually about 1800−1950 μs after gas pulse), and the width—how long to pulse the microwaves (~1 μs).[13] Next, we need to control when to trigger the oscilloscope to collect the molecular response. Only a delay is required because the collection width is controlled with the oscilloscope itself. Using the multiplex feature of the delay generator, we can use two channels to control each of these pulses and synchronize them all to the gas pulse. Because we are using an 8-channel delay generator and each microwave pulse/collection event takes two channels while the gas pulse takes another channel, three microwave pulses per gas pulse are achievable without any additional electronics.

The settings of the delay generator are such that there is little-to-no cavity ringing detected in the instrument from the excitation and only the molecular response is monitored. During the molecular interaction period, if the bandwidth in the cavity is in resonance or close to resonance with a rotational transition, excitation occurs. The radiation couples to the molecule through a permanent electric dipole moment. Each molecule that is excited has its dipole align with the electromagnetic field in the cavity and the molecules begin to rotate in unison. This interaction satisfies the $\pi/2$ condition where the populations of the lower and upper state are equal.[34] When the pulsing of the radiation ends, the molecules relax randomly back to thermodynamic equilibrium, which results in an exponentially decaying time-domain FID.[13,28,29]

The FID decoherence time is molecule dependent but is usually finished in <1 ms. In this experiment, FID data are collected for 100 μs and excited shortly after (as previously described), in order to get a signal-to-noise advantage. The FID signal is low-noise amplified and mixed down to 30 MHz using an image rejection mixer and the original microwave synthesizer output. Any molecular signal present will be located at 30 ± ΔMHz, where the Δ is the offset of the molecular signal from the tuning frequency. This signal is amplified again with a 30 MHz amplifier (low noise is better, but not necessary) and the resultant signal is sent to the oscilloscope for interpretation. This signal, as previously stated, is collected in the time domain and fast Fourier transformed using a Hanning windowing-type into the frequency domain where the resultant spectra appears as a Doppler doublet (see abstract figure). As mentioned earlier, this doublet arises in the experiment because the nozzle orientation is parallel to the microwave propagation. Amazingly, this orientation improves both signal AND resolution.[28,29]

The oscilloscope is a key piece of instrumentation in this setup. Multiple pulses in very quick succession require the oscilloscope to be triggered rapidly and store these acquisition events separately. Most oscilloscopes can do this through segmented memory, but sometimes oscilloscopes have hardware limitations on the number of acquisitions that can be stored in this way or the data cannot be exported, so be careful. We chose the Tektronix TDS5054B because it could be found very inexpensively in the second-hand market and it has the extra feature of FastFrame technology, which allows one to do math averaging and Fourier transformations directly on the segmented memory. These are just conveniences and not requirements as these features could be achieved with computers containing free scripting software like PYTHON. In the choice of an oscilloscope, the most important feature (other than bandwidth) is that the user be able to utilize, store, and access triggers captured in the segmented memory so that information can be gathered and stored on a fast time scale.

Extended Rotational Resources for the Physical Chemistry Community

It is appreciated that even at the reduced budget for building a spectrometer presented here that there still could exist a financial and/or technical burden to overcome in order to execute this laboratory. In these situations, an instructor wishing to implement this (or another) rotational spectroscopy laboratory into their curriculum is encouraged to reach out to the authors as there are multiple resources they can provide.

First, corresponding author Grubbs is overseeing the construction of a state-of-the-art CP-FTMW experiment designed to be used with software remotely, giving the student(s) complete control of the instrument with the exception of loading the sample. The home institution would only be responsible for the consumables cost of sample. The instrument is still in the design and construction phase but should be available to the public for scheduling and use in approximately 3 years. Second, the authors are happy to provide resource sharing of the cavity FTMW instrument described here for benzonitrile or any other molecular sample capable of study within the instrument's functional range of 3−18 GHz as long as, again, consumables costs are covered. This solution is less hands-on because this instrument does not and will not feature remote accessibility, but still provides significantly more exposure to rotational methods than are typically provided.

■ HAZARDS AND SAFETY PRECAUTIONS

Along with the anticipated increase in signal and relation to astrochemistry, benzonitrile was chosen due to its low expense and toxicity. Standard safety equipment for a teaching laboratory, i.e. safety glasses/goggles, closed-toed shoes, and gloves are all that are required when handling the chemical. For our laboratory execution, either the instructor or teaching assistant preloaded the sample into the inlet line, but it may be desirable that other versions of the exercise have students load the sample as an additional hands-on experience. This scenario would be the most hazardous since the user must relieve the pressure in the backing gas line, load the sample, and then re-establish the backing pressure in the line without causing the sample to shoot into the solenoid valve or ejection of the sample from the line due to inadequately tightened tubing. Once loaded, the instrument does not require safety equipment to operate, but caution should always be observed in a chemical lab space.

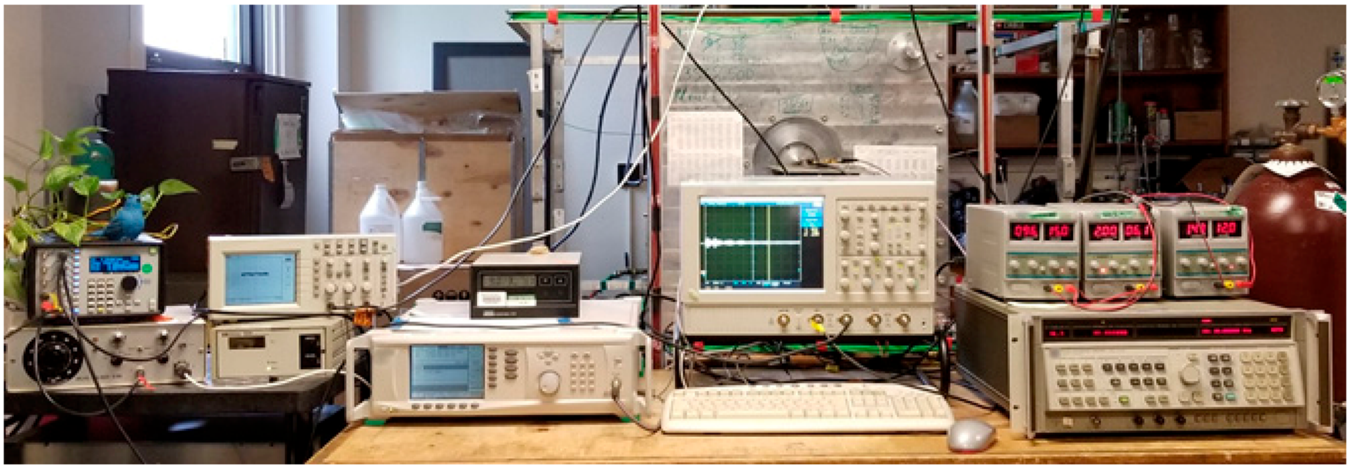

Figure 3. Photo of the control center for the FTMW instrument. The vacuum chamber with Helmhotlz coils is shown in the background. The only item on when students arrive is the vacuum gauge pressure readout (third modular component from top left).

STUDENT USE OF INSTRUMENTATION IN LABORATORY

An important aspect of the laboratory exercise is that students use the instrument in its entirety with the exceptions of loading sample and turning on the vacuum system (these are not included as efforts to save time). This is inclusive of turning on the instrument electronics, tuning to the correct frequency of light with the correct mode, and collecting data. While much of the sequence of events can be automated (and are automated when the instrument is used for research purposes), it is not utilized in the undergraduate laboratory. The reason for this is 2-fold. The first reason is to show the students the underlying principles associated with the aspects of building and maintaining an instrument. Most instruments they will encounter as chemists are purchased directly from a vendor to be used as designed and programmed by the end user. In this situation, however, the student is in control and must be cognizant of most aspects of the instrument's design in order to arrive at the desired spectroscopic result. For example, the tuning of the spectrometer is done by hand using a gear box and a linear actuator. The setup could be automated with a stepper motor and encoder with some programming, but for the lab it is not, so that the students understand that small movements of the mirrors largely affect the data being collected.

After turning on all electronics and while performing the lab, Figure 3 is what the students see. This is to show that interaction with instrumentation is just as important of a skill as performing synthetic chemical tasks and should be treated with the same level of caution and care. Step-by-step procedures of the process for student interaction with the instrument are also found in the Supporting Information. The usefulness of this approach is discussed in the next section.

DISCUSSION

Although no formal polling has been taken, overall, the students find this lab to be a very engaging experience that is different from their many other chemistry lab experiences. As students generally find quantum mechanics and statistical thermodynamics to be some of their most difficult subjects,[42] this result must be due to their direct interaction and complete control of the instrument. Students in this lab, as a whole, tend to approach the laboratory exercise with vigor and intrigue as it is an unusual, but fun experience for them to effectively have domain over all aspects of a built instrument. In many other instrument laboratory environments, this interaction is highly regimented so that the student has little-or-no license to explore the functionality of the instrument. Students will typically, in these settings, follow a series of carefully planned instrument instructions because that is how they get their desired data while also minimizing the risk of damaging any equipment. In this laboratory, just about everything is controlled by the student and they have to get the spectra to come in as strong as they feel is necessary in order to perform a successful laboratory. If they're unsuccessful or are not able to get spectra at all of the prescribed tuning frequencies, they have to go back and continue their efforts. This action gives them extra investment in the laboratory. Their enjoyment of the instrument side of the exercise is also shown by their general tendency to do well in the experimental portion of the final lab report, which is a typed, journal format-style exercise.

Most students struggle, however, with the calculations and fitting the spectra using Pickett's SPFIT/SPCAT software. This software, although robust, has a steep learning curve.[43] Although students are warned that this is a difficult aspect to the lab, if they do not allow adequate time, they may not understand what they are doing, why they are doing it, or the connection and relationship between the measured spectra and the molecular structure. They also struggle with the concept of nuclear electric quadrupole coupling and its effects even though it is covered in a prelab lecture. Other software fitting routines have been considered, but Pickett's software suite is still considered the gold standard fitting package[44] for the molecular spectroscopy community due to its precision, accuracy, and flexibility, so it only makes sense to continue to train students using these common molecular spectroscopy tools. Finding the balance with these problems will be a focus of future implementations of the laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c00934.

Example brief descriptions with file formats that can be customized for your material; details of Balle-Flygare instrument; copy of laboratory handout for students with questions (PDF, DOCX)

AUTHOR INFORMATION

Corresponding Author

G. S. Grubbs, II − *Department of Chemistry, Missouri University of Science & Technology, Rolla, Missouri 65409, United States;* orcid.org/0000-0002-1162-8819; Email: grubbsg@mst.edu

Authors

Amanda Duerden − *Department of Chemistry, Missouri University of Science & Technology, Rolla, Missouri 65409, United States*

Nicole Moon − *Department of Chemistry, Missouri University of Science & Technology, Rolla, Missouri 65409, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jchemed.0c00934

Notes

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