A Solid-State Theoretical and Experimental Analysis of Nitroguanidine and Gunshot Residues

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Abstract

Low-frequency spectroscopic techniques, including terahertz time-domain spectroscopy and THz-Raman spectroscopy, are used in conjunction with solid-state density functional theory simulations to investigate the vibrational modes of the explosive propellant nitroguanidine and three gunshot residues. Terahertz spectroscopy and low-frequency Raman spectroscopy are used to probe these small organic crystalline systems because the low-frequency (sub-200 cm\(^{-1}\)) spectra for these systems are either, in the case of terahertz, not yet published in the spectral range obtained in this work, or in the case of Raman, not focused on in the literature. Low-frequency spectra and the corresponding solid-state density functional theory simulations can provide information on the vibrations and torsions within the crystal that are unique to the system and can be used to detect and identify these organics. Since all the organics studied in this work are found in dangerous materials, having the spectral fingerprints available in the low-frequency range to expand the reference database can facilitate the detection of nitroguanidine-containing explosives or help identify the presence of gunshot residues at the scene of a crime, or on a suspect, when a firearm was discharged.
A SOLID-STATE THEORETICAL AND EXPERIMENTAL ANALYSIS OF NITROGUANIDINE AND GUNSHOT RESIDUES

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B.S. United States Coast Guard Academy, 2012

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CHAPTER 1: Low-Frequency Vibrational Spectroscopy in the Solid State

1.1 Introduction

1.1.1 What is Low-Frequency Spectroscopy?

Low-frequency spectroscopy refers to the region of the electromagnetic spectrum that falls between the infrared region and the microwave region as shown in Figure 1.1. This region is called the terahertz (THz) region where 1 THz corresponds to 33 cm$^{-1}$.

The THz region is commonly called the “final frontier” of the electromagnetic spectrum. It wasn’t until the 1960’s that investigations were completed using what at the time was called “far-infrared” spectroscopy [2] where researchers began delving into this yet unused region. In the 1970’s, the first papers were published using low-frequency Raman (now called THz-Raman) spectroscopy [3, 4]. Then, in the 1980’s, the development of ultrafast pulsed lasers and photoconductive (PC) antennas paved the way for the first THz wave emitter and detector set-up [5-7].

Figure 1.1. A chart of the electromagnetic spectrum [1].
How did scientists send a man to space before being able to work in the THz region? The THz region is unique and was hard to access because of where it lies in the electromagnetic spectrum. It sits right between the region generated by electronics (microwaves, etc.) and the region generated by optics (infrared, etc.). These domains overlap in the THz region, making THz radiation hard to generate and control since the conventional methods and assumptions made that govern electronics and optics don’t necessarily apply in the THz region [7, 8]. It took the development of new technology and methods to finally be able to work in that region, technologies that are constantly being improved upon as the field of THz spectroscopy continues to grow.

1.1.2 Why Terahertz Spectroscopy?

Waves in the THz region have low photon energies, making THz radiation non-ionizing and non-destructive. Therefore, the use of THz spectroscopy preserves sample integrity. Additionally, THz waves are easily absorbed by water. While this makes obtaining clean spectra difficult, this means THz waves cannot penetrate the human body very far, if at all, making THz waves safe not only for the sample, but for the user as well [7].

Water is not the only molecule that absorbs THz radiation. The second important advantage of THz waves is, at THz frequencies, many molecules exhibit strong absorption due to dipole-allowed rotational and vibrational transitions. These transitions are unique to the molecule and allow for spectroscopic “fingerprinting” using either frequency-domain or time-domain spectroscopy [7]. Using these fingerprints results in the characterization of these molecules, even granting the ability to differentiate between molecules of similar structure [9,
These same principles apply not only to unique vibrations, rotations, and internal molecular torsions within a single molecule, but to motions in solids as well [11-13]. Because these low-frequency vibrations and torsions are unique, they can be used to tell two solids apart that are comprised of the same molecule but where each solid is made up of molecules in different packing arrangements, a relationship known as polymorphism [13, 14].

Low-frequency spectroscopy is now used on a wide range of systems and for several purposes. The following examples are just a small sampling of the research currently being done with or the real-world applications of low-frequency spectroscopy: organic and biological systems [9, 10, 15-17], polymers [12, 18, 19], forensics [20-22], illicit drugs and explosives detection and identification [22-29], pharmaceuticals [13, 30], and astrochemistry [31, 32].

1.1.3 Low-Frequency Spectroscopy in This Work

The research projects highlighted in this work have applied THz absorption and THz-Raman scattering to the explosive propellant nitroguanidine (NQ) and to a series of gunshot residues.

Nitroguanidine has been investigated by this group in the past [33]. This molecule is being re-investigated because five years have passed, and in that time both the spectroscopic technology as well as the theoretical methods have improved dramatically. This work presents new experimental THz spectra of almost twice the bandwidth as previously published. Additionally, this work applies new theoretical methods in modeling NQ, methods that were not yet available five years ago. Using these updated methods, this work re-evaluates the conclusions drawn from the limited spectral data in the previous work. This analysis and
A gunshot residue is a compound resulting from the reaction of the gunpowder in the ammunition cartridge during the discharge of a firearm. Using low-frequency spectroscopic methods is important and appropriate in characterizing these residues because the residues are found in particulate, or solid, form [34]. Little data is available in the literature on the low-frequency spectral fingerprints of the gunshot residues examined in this work [35, 36]. Therefore, identifying and characterizing the spectral fingerprints of these gunshot residues will help build the database of available information for crime scene investigations. Three gunshot residues were investigated in this work and are discussed in Chapter 3 of this thesis. However, as a snapshot, Figure 1.4 shows the spectral results of THz-Raman for one of the gunshot residues, ethyl centralite (EC).
Taking the experimental low-frequency spectra of these systems provides just that, spectral data with peaks with no further information about the solid of interest. In order to characterize the peaks observed in the experimental spectra, computational models are needed to provide the necessary insight. The systems investigated in this work are all crystalline, therefore requiring an appropriate theoretical method that will properly model these solid-state systems. The theoretical method used in this group to model these organic molecular solids and to assign vibrational frequency modes in the experimental spectra is solid-state density functional theory (SS-DFT).

1.2 A Discussion of Solid-State Theory Used in This Work

Density functional theory has its roots in Hohenberg and Kohn’s theorems that connect Schrodinger’s equation with electron density. These theorems connect energy with electron density and allow for the ground state energy of a system to be expressed as a function of the electron density [37] and are applied using the mathematical devices described in this section.
1.2.1 Functionals

A functional is similar in concept to a function, but where a function plugs in a value of a variable to give or define a number, a functional uses a function as the variable to define a number. With this in mind, the first theorem of Hohenberg and Kohn can be paraphrased as “the ground-state energy from Schrodinger’s equation is a functional where the function defining electron density is plugged in to give a numerical value of energy” (hence the name density functional theory). Now, if this functional is written out in terms of single-electron wavefunctions (which collectively define the electron density), the total energy can be defined by a known energy term \( E_{\text{known}} \) and an unknown energy term \( E_{\text{XC}} \). The known term includes the electron kinetic energies, the Coulomb interactions between electrons and nuclei, the Coulomb interactions between electrons, and the Coulomb interactions between nuclei. The unknown term is the exchange-correlation functional and includes all the remaining interactions [37, 38].

Hohenberg and Kohn may have shown an exact electron density functional exists, but it is not yet known because the exchange-correlation functional is not known. Therefore, there are functionals that provide approximations to this exact functional. The starting point for these approximations is based on the one system where the exchange-correlation functional can be derived exactly, the uniform electron gas [37-39]. At first glance this may not seem helpful because it is the change in electron density that shows the chemistry happening within a system. However, using the exchange-correlation functional from the uniform gas to define the electron density at each position in a solid system allows for a way to define the Kohn-Sham equations. This approximation is known as the local density approximation (LDA) [37, 39-41].
The next step in adding more physical information to the approximation of the exchange-correlation functional is incorporating how the electron density is changing locally in addition to the local value of the density. This correction gives rise to the generalized gradient approximation (GGA) functionals. Because there are different mathematical means of incorporating the gradient of the electron density into the functional, there are different GGA exchange functionals [37, 39-41]. An example of a GGA functional that has also been used in this work is PBE (Perdew, Burke, and Ernzerof) [42].

More complicated functionals have also been developed that derive the exact exchange energy from the exchange energy density. The difference between these types of functionals and ones previously discussed is that these are non-local. In other words, the electron density for all spatial locations must be known to solve for the exchange energy at one location. Functionals that combine this exact exchange energy and a GGA exchange functional are called hyper-GGA functionals. The most common of these functionals, and one that has also been used in this work, is B3LYP (Becke 88 [43], Lee-Yang-Parr [44, 45]). This functional is also called a “hybrid” functional, which is a class of functionals that include exact exchange.

Another consideration in the approximation of the exchange-correlation functional are factors such as Van der Waals forces or dispersion forces. The Grimme dispersion correction (D3) [46] is used in this work as the dispersion correction to functionals such as PBE and B3LYP to account for these factors. Another class of functionals, range-corrected functionals, account for long-range/short-range electron-electron interactions within the functional itself. An example of this class of functional and one functional that is used in this work is SC-BLYP which is the short-range corrected [47, 48] BLYP functional (B88 [49] and LYP [44]).
1.2.2 Basis Sets

The second piece needed to describe the electrons in a system is the definition of the molecular orbitals of that system. In DFT calculations, the molecular orbitals are broken down to be defined mathematically. To accomplish this, the linear combination of atomic orbitals (LCAO) approximation is applied. LCAO theory works such that a molecular orbital is described by a linear combination of a set of base functions called a basis set. This method is an approximation because an exact basis set would need to be a complete basis set (infinite), something that is not computationally possible. Therefore, basis sets used in DFT are finite with the size of the basis set used in calculations dependent on the balance needed between accuracy and computational time.

Atom-centered basis sets, the type of basis sets used in this work, are comprised of functions that are centered on the atoms within the system. The initial method used to mathematically define atomic orbitals (AO) in terms of these basis sets was to use basis set functions that corresponded to something already solved exactly, the hydrogen atom. This initial approach led to the use of Slater-type orbitals (STO’s) as functions to describe atomic orbitals [38]. However, while accurate, calculations involving STO’s led to integrals that were difficult to solve, so another type of function was needed.

In 1950, Gaussian functions were introduced as an alternative option [39, 50] and had the form centered on atom $b$ where $N$ is the normalization constant, $x, y, z$ are the cartesian coordinates with origin at the nucleus of $b$, $\alpha$ is the orbital exponent, and $r$ is the distance to the nucleus of $b$:
At first glance the use of a single function or Gaussian-type orbital (GTO) to describe an AO presents two problems. The GTO doesn’t have the correct radial shape, nor does it have radial nodes [38, 39]. The solution to both issues was to use a linear combination of GTO’s instead of a single function. When a basis function is defined as a linear combination of GTO’s, that basis function is called “contracted” and the GTO’s that make it up are called “primitive”. This approach solved both problems as the linear combination provided a better fit of the basis function to the STO and the coefficients could be positive or negative, allowing for nodes [38].

A basis set that uses a single basis function for each type of orbital is called a single-\(\zeta\) or a “minimal” basis set. To introduce more flexibility into the basis set, more functions can be used to describe each AO. In the case of double-\(\zeta\), two basis functions are used to describe the AO instead of one. Similarly, in triple-\(\zeta\), three basis functions are used and so on. However, equally describing all the orbitals may not provide the most accurate chemical picture because not all electrons are involved in bonds. A split-valence basis set addresses this issue. In a split-valence basis set, the valence orbitals are each split into many basis functions while the core orbitals are each defined by a single (contracted) basis function.

These atom-centered basis sets have the innate issue that they are atom-centered but need to be used to describe chemical bonds. To allow the basis sets to account for bonds, polarization is introduced into the sets through the addition of basis functions corresponding to angular momentum that is one level higher than the valence orbitals [38, 39]. As two examples
of accounting for polarization into a basis set, hydrogen would have a \( p \)-orbital basis function added to its basis set and carbon would have a \( d \)-orbital basis function added to its basis set.

One of the basis sets used in this work is presented here as an example of the implementation of the basis set corrections discussed in this section. In the case of the basis set 6-311G(d,p) [51], “6” is the number of primitives used in the contracted core, “3” “1” and “1” are the numbers of primitives used in the valence functions, “G” designates the use of Gaussian functions, and “(d,p)” designates the use of polarization functions where a \( d \)-orbital is added to all second row elements and a \( p \)-orbital is added to hydrogen.

1.2.3 Reciprocal Space

To perform calculations on solid-state materials, the first basic assumption made about those materials is that they are periodic in space, meaning they are a lattice of repeating units [52]. Therefore, the structure of the bulk crystal is considered a lattice of infinite “building blocks” or unit cells that, when repeated, completely fill all of space and reconstructs the full structure. To find these unit cells, the symmetry of the crystal lattice is used to simplify the bulk crystal down to its most basic unit that still holds all the information about the crystal [52]. The boundaries of the unit cell then become the calculation’s periodic boundary conditions. Instead of a calculation moving through infinite cells, once the calculation meets a periodic boundary, it will enter the same unit cell again [39] (like Pac-Man when he reaches the end of his screen, he pops right back into it on the other side with everything in the screen remaining the same). Reducing the crystal down to a unit cell with periodic boundary conditions reduces the number of calculations needed since the unit cell is an accurate representation of the entire crystal.
Although the system can be simplified to a single unit cell for calculations, the system is still periodic. Therefore, the solution of the Schrodinger’s Equation for this system must also be periodic. To ensure the solution is periodic, it must satisfy Bloch’s Theorem [37, 52] and will have the form:

$$\phi_k(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_k(\vec{r})$$  \hspace{1cm} (1.2)

In this general form, $u_k(\vec{r})$ is periodic in space with the same periodicity as the unit cell and $e^{i\vec{k} \cdot \vec{r}}$ is a plane wave function with wavevector $\vec{k}$ and position vector $\vec{r}$. The periodicity of the system is reflected in the position vector $\vec{r}$ as follows with $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ as the unit cell lattice vectors with integer coefficients $n_i$ [53]:

$$\vec{r} = \vec{r} + n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$  \hspace{1cm} (1.3)

The space of the $\vec{r}$ vector is called real space and the space of the $\vec{k}$ vector is called reciprocal space or $k$-space [37]. Equivalent to how real space was defined with lattice vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, reciprocal space can be defined by using reciprocal lattice vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ that satisfy $\vec{a}_i \cdot \vec{b}_j = 2\pi$ if $i = j$ and equals 0 otherwise [37, 52]. Therefore, the reciprocal lattice vectors are defined as:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$  \hspace{1cm} (1.4)

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)}$$  \hspace{1cm} (1.5)

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}$$  \hspace{1cm} (1.6)
Using these vectors, the unit cell in real space can be represented in reciprocal space [37, 52, 54]. Additionally, because the real space system is periodic, the corresponding reciprocal space system is also periodic with the reciprocal space unit cell as the “building block”. In reciprocal space, this unit cell is called the Brillouin zone (BZ) [37, 52].

When conducting a DFT calculation, the BZ plays a key role because it holds all the possible values of $k$ of the system. Any values of $k$ outside of the BZ are redundant because of the periodicity of the zone. These $k$ points in reciprocal space are integrated over to calculate the energy of the system in real space. To simplify this DFT calculation further, symmetry is once again applied and used to reduce the BZ to the irreducible Brillouin zone (IBZ). The IBZ holds less $k$ points, but still can accurately represent the BZ because of symmetry [37]. Therefore, the computational resources needed to integrate over the necessary $k$ points is reduced because less $k$ points are needed to represent the system mathematically.

1.3 Computational Methods with CRYSTAL17

The software package CRYSTAL17 [53] was used to conduct the SS-DFT calculations completed in this work. CRYSTAL17 applies $ab\ initio$ treatment of periodic systems using DFT and conducts calculations in the IBZ (described in the previous section). All crystalline systems analyzed in this work followed the same computational process that will be described in this section. The starting geometry used for initial system calculations, including shrinking factors and geometry optimizations, comes from the crystal structure of that system either published in the literature (from the Cambridge Structural Database [55]) or experimentally solved at Syracuse University.
1.3.1 Choosing a Functional and Basis Set

With several classes and types of functionals to choose from, it is important to discuss why certain functionals and basis sets were used in this work and how the balance between accuracy and computational time was met. The level of accuracy of a functional on a given system isn’t necessarily guaranteed by how complicated the functional is, so choosing a range-corrected without looking at a GGA with a dispersion correction may not be the best route. Concerning basis sets, a bigger basis set may be more accurate, but the calculation may not run with the choice of functional or the calculation may take an extremely long time to complete.

As mentioned above, PBE, B3LYP, SC-BLYP, as well as several other functionals were used in this work. Of the functionals, PBE with a dispersion correction was used as an entering argument in all cases because it historically worked well with systems modeled by this group [56, 57]. As for the basis set, moderate basis sets were chosen that were known to be compatible with PBE such as 6-311 G(d,p) or Ahlrichs VTZ with polarization [58]. If the computational resources were available, a large basis set such as DEF2-TZVP [58, 59] was used with PBE. If PBE did not provide an accurate model, hybrid functionals (such as B3LYP or PBE0 [60]) were the next to be considered and were preferably run with the same moderate basis sets with the understanding that the time needed for calculations using the hybrid functionals would increase by a factor of approximately two.

1.3.2 Shrinking Factor Calculation

The first step when modeling a system in CRYSTAL is to determine the appropriate number of k points in reciprocal space needed to accurately describe the system. The factor
that determines the number of points used within the calculation is called the shrinking factor (IS) and is manually entered into the input file. When testing a new system, several shrink calculations are run with increasing IS until the energy difference between two successive calculations is less than $10^{-10}$ hartree. A visual representation of two different IS values and the resulting $k$ points from the Pack-Monkhorst method [61] is shown in the following figure from the CRYSTAL17 manual, page 109 [53]:

![Figure 1.5](image)

**Figure 1.5.** Representation of the reciprocal lattice cell of 2D graphite, the first BZ (hexagon) and the IBZ (dark grey) with the sampling of points according to a shrink factor of 3 (left) and 6 (right).

### 1.3.3 Structural Optimization Calculation

Once an appropriate IS is found, the next step in mathematically simulating a system is finding the equilibrium, or “optimized”, geometry. This geometry optimization process finds the local minimum on the potential energy surface near the initial or starting geometry [50]. In a
full optimization, the system can completely relax with the symmetry of the unit cell as the only limitation. This process is a “zero temperature” approach, meaning that the system’s optimized geometry is calculated for the system at 0 K [37, 53] and represents the total electronic energy of the solid.

During the calculation, the energy and its gradient are calculated for the current molecular positions. The molecular positions are then changed slightly by following the gradient descent to lower the energy of system, and the energy and gradient are calculated again from the new molecular positions. Based on the results of this new calculation, the molecular positions are changed to lower the energy further. This cycle of calculations is repeated as needed until the change in the energy of the system between optimization steps is below set tolerances, which in this work is $10^{-8}$ hartree for optimizations.

### 1.3.4 Frequency Calculation

The property of interest in this work is the set of low-frequency vibrations of the system and requires the optimized geometry of the system to be calculated first. The simulated vibrations give the curvature of the potential energy surface near the minima found by the optimization. Calculating the frequencies of the optimized structure also acts as a check on the theoretical model. If the simulated spectrum and the spectrum obtained experimentally don’t match or line up, then the model is not an accurate representation of the system. On the other hand, if the model and experimental spectra do match, then the model is a good representation of the system and can be used to analyze the molecular motion that results in the frequencies seen in the experimental spectrum.
In CRYSTAL, a frequency calculation also uses a “zero temperature” approach just as it did during the optimization calculation. The vibrations themselves are treated using the harmonic approximation. A Hessian matrix is built using the second derivatives of the energy with respect to the optimized geometry. This matrix is then used to form the mass-weighted force-constant (or mass-weighted Hessian) matrix, which in turn is used to derive the equations of motion for the system. To solve these equations of motion, the mass-weighted Hessian is diagonalized to obtain the eigenvalues and eigenvectors of the system. The eigenvalues are converted to frequencies (cm\(^{-1}\)) and the eigenvectors define the normal modes corresponding to those frequencies [37, 53].

1.4 Instrumentation

Even though there are sophisticated computational methods for calculating system properties in the solid state, experimental data is still at the core of learning more about these systems. For example, without the initial crystal structure of a system, the CRYSTAL software has no reference point of where to start for shrinking factor calculations or geometry optimizations. Additionally, the experimental vibrational spectra are needed to check that those calculations are accurate. This section discusses the different experimental methods used to obtain the data that validated the corresponding theoretical models and was then analyzed using those models. Two different methods were used to obtain the experimental data analyzed in this work: Terahertz Time-Domain Spectroscopy and Low-Frequency Raman Spectroscopy.
1.4.1 Terahertz Time-Domain Spectroscopy

The basic set-up for a Terahertz Time-Domain Spectrometer (TDS) consists of a femtosecond (fs) laser, an emitter photoconductive antenna, a detector photoconductive antenna, and an optical delay line. The fs laser is split into two beams with one beam going to the emitter and one beam going to the detector. Both the emitter and detector photoconductive (PC) antennae consist of two metal electrodes deposited on a semi-conductor (ex: GaAs) with a physical gap between them [7, 62].

To generate a THz pulse, voltage is applied across the gap of the emitter PC and creates a well of electrical energy in the gap area. The laser pulse, with photon energies exceeding the semi-conductor band gap, creates a fast “spark” across the gap and releases a THz pulse [7, 62]. On the other side, the detector PC antenna has the same construction but is connected to a current sensor. The laser pulse is also applied to the detector to put electrons in the conduction band, electrons that are then ready to be accelerated by the incoming THz pulse and create a current. The sensor then measures the amplitude and phase of the electric field generated by the incoming THz pulse.

The waveform is captured by measuring the electric field generated by the THz pulse on the detector at various parts of the pulse by delaying the laser pulse. To illustrate, the THz pulse is generated and passes through the sample. If the laser pulse happened at the same time on the detector, it would take a snapshot of the beginning of the THz pulse (both at 0 ps). On the next THz pulse, the laser pulse is delayed by 0.1 ps and takes a snapshot of the THz pulse 0.1 ps into the THz pulse hitting the detector. On the next THz pulse, the laser pulse is delayed by
another 0.1 ps to snapshot 0.2 ps into the THz pulse hitting the detector. The process continues in this way until the entire THz pulse is captured in a series of 0.1 ps snapshots and plotted to give the waveform as a function of temporal delay between the laser pulse and THz pulse.

To extract information about a sample, two waveforms must be taken: one of the sample and one of a reference (free space or a “blank”). These waveforms in the time-domain are then converted to the frequency-domain using a Fourier transform [63] to give the spectral distribution. The spectral response of the sample is then obtained by taking the ratio between the magnitudes of the transformed waveforms to give the absorption coefficients [7].

The spectra obtained in this work were acquired from two different commercial instruments the group had on loan. One was a Toptica TeraFlash™ Time-Domain Terahertz Spectroscopy Platform (Munich, Germany) shown in Figures 1.6 and 1.7. The other was a Menlo Systems TERA K15 Time-Domain THz Spectrometer (Martinsried, Germany) shown in Figure 1.8.

Figure 1.6. Set-up of the Toptica instrument with the cryostat and purging bag.

Figure 1.7. Set-up of the Toptica instrument with the cryostat and off-axis paraboloid mirrors.
1.4.2 Low-Frequency Raman Spectroscopy

The Raman spectroscopy instrumentation used in this work is the ONDAX (Monrovia, California) low-frequency THz-Raman XLF-CLM unit with a laser excitation wavelength of 784.7 nm and fiber-coupled to an ANDOR (Belfast, Northern Ireland) Shamrock SR-750 spectrometer with a CCD-18171 iDus camera (DU416A-LDC-DD). What makes this instrumentation unique is its ability to capture the low-frequency (below 100 cm$^{-1}$) spectra of samples instead of the higher frequency ranges commonly seen in literature. The ONDAX system employs a SureBlock$^\text{TM}$ ultra narrow-band notch filter that allows for a transition width of $\sim$$10$ cm$^{-1}$, improving the rejection of the Rayleigh peak and making the low-frequencies down to $\sim$$5$ cm$^{-1}$ available for observation.
The experimental set-up used for THz-Raman data collection is shown in Figure 1.9. Because the sample was housed in the cryostat for both room and low temperature scans, the sample housing unit that originally came with the ONDAX laser was removed to allow the laser to reach the cryostat. Because the original housing was removed, the laser and sample were no longer isolated from outside light contamination. Therefore, the lights in the laser lab were turned off during all data collections to prevent atomic emission peaks from the fluorescent overhead lights from appearing in the sample spectra.

*Figure 1.9.* Set-up for Raman data collection including the cryostat (left), Ondax laser (center) and Andor spectrometer (right).
1.5 Data Work-Up

1.5.1 Experimental Data Work-Up (THz)

The data “output” of both commercial THz-TDS instruments was a text file with the signal delay in picoseconds (ps) and the THz signal in arbitrary, but consistent, units of current. For the Menlo instrument, three separate waveforms were taken of the sample and of the blank and were averaged to give the sample averaged waveform and the blank averaged waveform. For the Toptica instrument, the respective waveforms were averaged in the provided vendor software. The waveform data was then truncated to remove THz pulse reflections that occur at interfaces within the experimental setup, or reflections that are not due to the absorption of the sample (the pellet reflection and the window reflection).

Once the data has been truncated, it is processed through a custom Python 2.7 [64] program written for transforming THz waveform data (Appendix 1). Within the program, the first step is to normalize the data to one. Within the pyspecdata library [65], the Blackman window [63] is defined as having a maximum value of one. To appropriately apply the window to the data, the data was first normalized to one before applying the Blackman filter.

The filtered data is then zero-padded [63] with the total number of points (after zeros were added) specified by the user (usually 16,384 total points) and Fourier transformed [7, 63, 66] into the frequency-domain using the functions available in the pyspecdata library. Finally, the ratio between the transformed blank and sample data is taken to give the THz spectra in optical density (OD) vs. wavenumbers (cm⁻¹).
Following processing, the experimental intensities (OD) need to be converted to units that can be directly comparable to the theoretical intensities from the corresponding calculation’s output file (in units of km/mol). To meet in the middle, both the experimental data and the theoretical data are converted to molar absorptivity coefficients, also known as extinction coefficients ($\varepsilon$, $M^{-1} \text{ cm}^{-1}$).

To convert the experimental units of OD to $\varepsilon$ ($M^{-1} \text{ cm}^{-1}$), the connection between the two values from Beer’s Law [38] is used:

$$A = \varepsilon(\nu)lC$$

where $A$ is the spectra intensities, $\varepsilon(\nu)$ is the extinction coefficient, $l$ is the path length, and $C$ is the concentration of the sample. Re-arranging Beer’s Law allows for the calculation of the extinction coefficient in terms of known variables:

$$\varepsilon(\nu) = \frac{A}{lC}$$

For the extinction coefficient units to be the desired $M^{-1} \text{ cm}^{-1}$, the concentration of the sample needs to be in units of mol L$^{-1}$ and the path length needs to have units of cm. Therefore, the concentration of the cylindrical pellets used in this work was calculated as follows:

$$C = 1000 \times \frac{m/(MW \times Z)}{\pi r^2 h}$$

where $m$ is the mass of the sample in g, $MW$ is the molecular weight of the sample with units g mol$^{-1}$, $r$ is the radius of the sample pellet in cm, $h$ is the thickness of the pellet in cm, $Z$ is the number of molecules in one unit cell, and 1000 is a conversion factor with units cm$^3$ L$^{-1}$. The mass of the crystal unit cell is accounted for by the multiplication of $Z$ and $MW$. 
1.5.2 Theoretical Data Work-Up (THz)

The frequency output file from CRYSTAL lists the normal mode infrared intensities in units of km/mol. While these units are commonly used in spectroscopy, they are not directly comparable to the experimental data which is unitless as optical density (OD). Therefore, the intensities need to be converted to the extinction coefficient ($\varepsilon$, M$^{-1}$ cm$^{-1}$). The extinction coefficients for the theoretical mode intensities are calculated in this work by the following equation:

$$\varepsilon(\nu) = \frac{100}{\ln(10)} \sum [L(\nu, \nu_0^i, \Gamma) \cdot A(i, \nu_0^i)]$$

(1.10)

where $A$ is the calculated (absolute) intensity of the $i^{th}$ mode in km mol$^{-1}$ and $L$ is the normalized Lorentzian. The first term $100/\ln(10)$ consists of a conversion factor (100, L km$^{-1}$ cm$^{-2}$) and a scale factor ($\ln(10)$, unitless) to ensure the correct units of the overall equation for the extinction coefficient (M$^{-1}$ cm$^{-1}$).

The normalized Lorentzian describes the shape of the spectral peak ensuring the area under the peak is unity, and is defined by:

$$L(\nu, \nu_0^i, \Gamma) = \left( \frac{\Gamma/\pi}{(\nu - \nu_0^i)^2 + \Gamma^2} \right)$$

(1.11)

where $\Gamma$ is the bandwidth (or full width at the half maximum height of the peak) in cm$^{-1}$, $\nu$ is the frequency in the spectrum in cm$^{-1}$, and $\nu_0^i$ is the frequency of the $i^{th}$ mode in cm$^{-1}$, resulting in overall units of cm$^{-1}$ for the normalized Lorentzian.
1.5.3 Experimental Data Work-Up (Raman)

Data in this work was acquired over a window ranging from -100 cm\(^{-1}\) to 300 cm\(^{-1}\) to ensure observation of both the Stokes and Anti-Stokes transitions, as well as to confirm proper placement of the Rayleigh line. During data collections, the importance of checking the Rayleigh line placement became apparent when an offset in the experimental spectra was discovered a few months after the new instrument was installed. The changing season, to include temperature and humidity, seemed to affect the system set-up just enough to cause an offset in the alignment of the Rayleigh peak with the laser wavelength. After troubleshooting, the error was resolved through the re-calibration of the spectrometer and will be prevented by subsequent re-calibrations of the spectrometer every 6 months. The custom-made set of spectrograph calibration procedures for this set-up is enclosed in Appendix 2.

The experimental Raman output was a text file with Raman shift (cm\(^{-1}\)) vs. intensity (arbitrary units) from -100 cm\(^{-1}\) to 300 cm\(^{-1}\). The Stokes transitions from this data (0 cm\(^{-1}\) to 300 cm\(^{-1}\)) were chosen to plot against the theoretical data due to the greater peak intensities compared to the Anti-Stokes transitions. This difference in intensities results from the Boltzmann distribution \([38, 66]\). The data was then normalized to one using the strongest peak that was not the Rayleigh peak.

1.5.4 Theoretical Data Work-Up (Raman)

The frequency output file from CRYSTAL lists the Raman intensities, in arbitrary units normalized to 1000.0, vs. the respective Raman-active mode frequencies (cm\(^{-1}\)). Similar to the work-up of the THz theoretical data, the Raman-active modes were then convolved using the
normalized Lorentzian (1.11) and absolute intensities of the modes to create a spectrum. The spectrum was normalized to one by the strongest peak to make it comparable to the experimental data.

1.6 References


65. Franck, J.M. *pySpecData 0.9.5*. 2017--; Available from: [https://pypi.org/project/pySpecData/0.9.5/#description](https://pypi.org/project/pySpecData/0.9.5/#description).

CHAPTER 2: Low-Frequency Vibrational Spectroscopy of Crystalline Nitroguanidine and Assignment via Solid-State Density Functional Theory

(Note: This chapter is written in the form of a publication and some information may be repeated from the previous chapter.)

2.1 Abstract

The low-frequency vibrations of the crystalline explosive propellant nitroguanidine were investigated experimentally first using both terahertz time-domain spectroscopy (THz-TDS) from 10 cm$^{-1}$ to 160 cm$^{-1}$ and THz-Raman spectroscopy from 5 cm$^{-1}$ to 300 cm$^{-1}$, and then modeled with solid-state density functional theory. The 78 K low-frequency THz spectrum obtained for crystalline nitroguanidine in this work almost doubles the bandwidth of the spectrum previously published. The bandwidth (160 cm$^{-1}$ vs. 100 cm$^{-1}$) revealed four new low-frequency peaks that required characterization. To assign the experimental spectral features to molecular vibrations, a comprehensive computational study was conducted in this work to find the theory that most accurately describes crystalline nitroguanidine. The computational analysis showed that several functional/basis set combinations offer reasonable simulations of the solid structure and vibrations, but none are able to achieve a level of agreement that completely removes peak assignment ambiguities. The theory providing the most accurate spectral simulation in this work is the range-corrected functional CAM-B3LYP with the DEF2-SVP basis set based on a fixed lattice geometry optimization.

2.2 Introduction

Nitroguanidine (NQ) is a commonly used explosive and component in artillery projectiles [1] and triple based gun propellant [2, 3]. Concerning the projectiles and explosives, NQ is one of the constituent compounds used to replace more sensitive compounds such as TNT and RDX
to make munitions less sensitive to external stimuli and safer to handle and deploy [1], implying that NQ will continue to stay a common component in future explosives. Therefore, it is important to understand NQ’s crystalline properties because of NQ’s prevalence in explosive compounds as well as its present in the environment where such explosives have been or will be used.

With NQ as a component of explosives, understanding its vibrational spectra in terms of its crystalline characteristics is important for detection and identification of NQ for both security and forensic analysis. Methods commonly used in these cases include terahertz radiation and Raman spectroscopy. Terahertz (THz) spectroscopy is both noninvasive and nondestructive, leading to its use for the detection and identification of explosive materials [1, 4-7]. Raman spectroscopy, and its use, has grown significantly in recent years in the field of forensics for the identification of compounds found at crime scenes to include explosive remnants such as gunshot residues [7-10].

Nitroguanidine, as an explosive and gunshot residue, has been characterized with THz and Raman spectroscopies and the resulting spectra have been published in the literature [4, 10, 11]. Beyond characterizing NQ spectra, a greater depth of understanding concerning the chemistry of NQ can be gleamed from theoretical models. While work in this area has been done [12-17], not as much as been published using solid-state, theoretical models.

In this work, new THz and Raman spectra are presented to provide and characterize vibrational data in an expanded spectral range not yet published. Here, terahertz data from 10 cm$^{-1}$ to 160 cm$^{-1}$ and Raman data from 5 cm$^{-1}$ to 300 cm$^{-1}$ were collected. These new spectra
will improve the extent of the database of available “fingerprint” information for NQ. In addition, an in-depth theoretical analysis is also presented to provide insight into these fingerprints and show how the model and its parameters were chosen. Solid-state density functional theory (DFT) was used to model the terahertz frequency vibrations in crystalline NQ where CAM-B3LYP/DEF2-SVP in particular showed marked improvement over previous work [4].

2.3 Methods

2.3.1 Experimental

Nitroguanidine (CAS #556-88-7) was ordered from Sigma-Aldrich (Lot #14321CDV, Catalog #N17351) and used as received with no additional purification beyond re-crystallization. Nitroguanidine crystals were grown from an aqueous solution saturated with NQ placed in a fume hood to evaporate off the water. The crystal structure of NQ was confirmed by powder and single-crystal X-ray diffraction and agreed with published results [4, 18].

2.3.1.1 Terahertz Measurements

The pellet for THz spectroscopic measurements was prepared by mixing a small amount of powdered sample (5.0 mg) into a non-absorbing matrix. The amount of sample used was dependent on the absorption strength of the sample. The matrix used for the pellet was polytetrafluoroethylene (PTFE) due to its weak low-frequency absorption in the THz frequency range of interest (below 200 cm\(^{-1}\)). The mixture of sample and matrix were then placed in a stainless-steel vial with a ball bearing and pulverized using a ball mill (Dentsply Rinn 3110-3A) to ensure the sample and matrix were a homogenous mixture. Approximately 550 mg of the
resulting mixture (or pure PTFE in the case of the “blank” pellet) was then pressed into a pellet using a hydraulic press (ICL EZ-Press 12) with a steel die with a pressure of 2000 psi to create a pellet 13 mm in diameter and 2 mm thick.

A cryostat was used to hold the sample and the blank during the THz spectroscopic measurements. This sample chamber was held under vacuum during the collection of the data. The external THz beam path was continuously purged with dry air to prevent any water absorption peaks from appearing in the sample and blank data sets. Spectra were obtained at room temperature (290 K) and liquid nitrogen cooled temperature (78 K) through polymethylpentene polyolefin resin (TPX) windows on the cryostat.

A Toptica TeraFlash Time-Domain Terahertz Spectroscopy Platform (Munich, Germany) was used to capture sample and blank waveform data using a 100 ps window and 20000 scans averaged together during the data collection by the software. Approximate scan times for each waveform collection was 20 minutes. The final data sets for the blank and the sample were then truncated to remove reflections from the pellet, resulting in a data range of 17 ps from the pulse to the cut-off. The spectra resolution for the truncated data was 1.96 cm\(^{-1}\). The laser source of this instrument is a 1560 nm femtosecond fiber laser with fiber-coupled InGaAs antenna photoconductive switches for THz generation and detection. The observed bandwidth was 0.3 - 4.8 THz (10 - 160 cm\(^{-1}\)).

2.3.1.2 Raman Measurements

The pellet for Raman spectroscopic measurements was made of pure sample. 250 mg of sample was pressed using the hydraulic press at a pressure of 2000 psi.
An ONDAX (Monrovia, California) low-frequency THz-Raman XLF-CLM unit, with a laser excitation wavelength of 784.7 nm and fiber-coupled to an ANDOR (Belfast, Northern Ireland) Shamrock SR-750 spectrometer with a CCD-18171 iDus camera (DU416A-LDC-DD), was used for data collection. The spectral resolution of this system set-up is 0.6 cm\(^{-1}\).

A cryostat was used to hold the samples and the blank during the Raman spectroscopy. This sample chamber was held under vacuum during the collection of the data. Spectroscopic measurements for Raman were taken at room temperature (290 K) and liquid nitrogen cooled temperature (78 K) using 225 acquisitions at 3 second exposure times through glass windows on the cryostat.

2.3.2 Theoretical

Solid-state DFT calculations utilizing periodic boundary conditions were performed with the CRYSTAL17 software package [19]. Several combinations of functionals and basis sets were tested to find the level of theory whose resulting simulations best matched the experimentally obtained data. Functionals tested included GGA functional PBE [20] and hybrid functional B3LYP [21, 22] (both with London dispersion correction (D3) [23]), and the range-separated hybrid functionals RSHXLDA [24], B97 [25], B97X [25], LC-BLYP [26, 27], SC-BLYP [26, 27], and CAM-B3LYP [28]. Basis sets used in these functional tests included cc-pVTZ [29], DEF2-TZVP [30, 31], Ahlrichs VTZ with polarization (VTZp) [32], 6-311G(d,p) [33], and DEF2-SVP [30, 32].

The low-temperature crystal structure from this group’s previous paper on NQ [4] was used as the starting coordinates for all geometry optimizations. Two different optimization types were conducted during the theory tests, full geometry optimizations and fixed-lattice
optimizations. In the full geometry optimization calculations, both the atomic positions and the unit cell dimensions were allowed to fully relax with unit cell symmetry as the only limitation. In the fixed-lattice calculations, the unit cell dimensions were held constant while the atomic positions were allowed to relax with unit cell symmetry remaining a limitation.

The resulting optimized geometries were used to calculate their respective vibrational spectra. These simulated spectra were then compared to the data collected experimentally in this work to evaluate the ability for various basis sets/functional combinations to reproduce structure and vibrations. The goal for these calculations was to find the combination of functional and basis set that most accurately described this system.

2.4 Results and Discussion

Nitroguanidine has an orthorhombic crystallographic unit cell (Figure 2.1) with NQ covalent bond data given in Table 2.1.

![Nitroguanidine: single molecule and unit cell](image)

**Figure 2.1.** Nitroguanidine: single molecule and unit cell [4].
Table 2.1. Experimental NQ covalent bond distances and angles [4].

<table>
<thead>
<tr>
<th>Bond</th>
<th>(Å)</th>
<th>Bond Angle</th>
<th>(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3-O1</td>
<td>1.252</td>
<td>O1-N3-O2</td>
<td>120.33</td>
</tr>
<tr>
<td>N3-O2</td>
<td>1.240</td>
<td>O1-N3-N2</td>
<td>124.35</td>
</tr>
<tr>
<td>N2-N3</td>
<td>1.337</td>
<td>O2-N3-N2</td>
<td>115.32</td>
</tr>
<tr>
<td>C1-N2</td>
<td>1.373</td>
<td>N3-N2-C1</td>
<td>118.88</td>
</tr>
<tr>
<td>C1-N1</td>
<td>1.316</td>
<td>N2-C1-N1</td>
<td>128.22</td>
</tr>
<tr>
<td>C1-N4</td>
<td>1.326</td>
<td>N2-C1-N4</td>
<td>112.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N1-C1-N4</td>
<td>119.31</td>
</tr>
</tbody>
</table>

2.4.1 Experimental Spectra

The THz spectra obtained in this work greatly improved on the range published previously [4], increasing the maximum bandwidth from 100 cm\(^{-1}\) to 160 cm\(^{-1}\) and revealing four new peaks above 100 cm\(^{-1}\) to investigate and assign.

As NQ was cooled from room temperature to 78 K, the observed THz peaks all shifted to higher frequencies and sharpened (Figure 2.2). This shifting is expected during cooling because as the temperature decreases, the unit cell contracts. This smaller unit cell results in more repulsive forces between neighboring atoms, creating a steeper potential energy surface and an increase in vibrational frequencies. The sharpening of the peaks during cooling is also expected and is described by the Boltzmann distribution. At lower temperatures there are fewer higher vibrational states populated, allowing for the observed peaks (Table 2.2) to be more representative of a single transition.
Table 2.2. Experimental THz frequencies and peak intensities of solid-state NQ.

<table>
<thead>
<tr>
<th>Frequencies (cm(^{-1}))</th>
<th>Peak Intensities ((\varepsilon, \text{M}^{-1} \text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.1</td>
<td>95.9</td>
</tr>
<tr>
<td>50.4</td>
<td>326.9</td>
</tr>
<tr>
<td>70.2</td>
<td>216.0</td>
</tr>
<tr>
<td>86.4</td>
<td>1814.5</td>
</tr>
<tr>
<td>97.2</td>
<td>664.1</td>
</tr>
<tr>
<td>100.7</td>
<td>1147.7</td>
</tr>
<tr>
<td>124.1</td>
<td>267.2</td>
</tr>
<tr>
<td>134.0</td>
<td>507.2</td>
</tr>
<tr>
<td>154.7</td>
<td>693.4</td>
</tr>
</tbody>
</table>

Figure 2.2. Experimental THz spectra of NQ obtained at 290 K (red) and 78 K (blue).
The Raman spectra also showed the same peak shifting and narrowing between the room temperature and cold temperature spectra (Figure 2.3).

![Experimental Raman spectra of NQ obtained at 290 K (red) and 78 K (blue) normalized to one.](image)

**Figure 2.3.** Experimental Raman spectra of NQ obtained at 290 K (red) and 78 K (blue) normalized to one.

### 2.4.2 Theoretical Investigation

The initial theory used in creating a model of this system consisted of PBE with the D3 dispersion correction (PBE+D3) and the DEF2-TZVP basis set due to the previous success of this combination in this group for providing accurate simulations. In this case however, the simulations of the NQ terahertz spectrum were less than satisfactory with the main concern being the splitting of the simulated peak at ~90 cm\(^{-1}\) (indicated with a star in Figure 2.4). The accurate reproduction of the NQ THz spectrum remained the main target of this work since the calculation of THz peak intensities (based on atomic charges) is more straightforward to calculate than what is required for Raman peak intensities (polarizabilities).
In an attempt to improve the simulation and address the splitting of the peak near 90 cm\(^{-1}\), B3LYP+D3 and VTZp were used together next to see how well a hybrid functional would model NQ. This level of theory has also been historically successful for work done by this group. Unfortunately, these simulations presented the same issue as before with the peak splitting as shown in Figure 2.5.
Having explored the initial theory, we decided to test a new family of functionals and began investigating range-separated hybrids to see how well they would model NQ. Because there were several functionals to test, geometry optimizations were run with a fixed lattice and both optimization and frequency calculations were conducted with the DEF2-SVP basis set to reduce the computational time, allowing for faster evaluation of how well each functional performed with this system.

The structures from each geometry optimization were compared to the X-ray crystal structure solved at Syracuse University [4] and the errors between each bond length were compared between the different functionals (Figure 2.6). The simulated frequencies were compared with the experimental spectrum obtained in this work (Figure 2.7).
Figure 2.6. Percent error of bond lengths from simulated structures of various functionals with DEF2-SVP as compared to X-ray diffraction measurements.

Figure 2.7. Simulation results of the THz vibrational spectra for various functionals with DEF2-SVP plotted against the experimental spectrum.
From these two comparisons, the functionals CAM-B3LYP, SC-BLYP, and wB97 were chosen as candidates for further testing with full optimizations with DEF2-SVP and both optimization and frequency calculations with a bigger basis set. These three functionals were chosen because of the correct relative intensities of the higher frequency modes around 140 cm\(^{-1}\) and the absence of excessive splitting in the peaks around 100 cm\(^{-1}\). Additionally, while CAM-B3LYP had the best spectrum compared to experiment, SC-BLYP and wB97 had the two lowest average errors in bond lengths.

The initial full geometry optimization results of SC-BLYP/DEF2-SVP and wB97/DEF2-SVP were not considered promising with the large errors present in the simulated lattice dimensions (Table 2.3). Therefore, SC-BLYP and wB97 were removed as candidates and had no further calculations conducted. Full optimizations and frequency calculations on the remaining functional CAM-B3LYP were conducted using the DEF2-SVP and 6-311G(d,p) basis sets. Based on the lattice dimension errors in Table 2.3 and the full optimization spectra results in Figure 2.8, CAM-B3LYP and its pairing with DEF2-SVP proved to be the most accurate theory applied thus far.

<table>
<thead>
<tr>
<th>Unit Cell Dimensions</th>
<th>Experimental Measurement (Å)</th>
<th>% Error with DEF2-SVP</th>
<th>% Error with 6-311G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CAM-B3LYP</td>
<td>SC-BLYP</td>
</tr>
<tr>
<td>a</td>
<td>17.643</td>
<td>-2.31</td>
<td>-1.96</td>
</tr>
<tr>
<td>b</td>
<td>24.883</td>
<td>-1.29</td>
<td>2.58</td>
</tr>
<tr>
<td>c</td>
<td>3.595</td>
<td>0.99</td>
<td>19.72</td>
</tr>
<tr>
<td>Volume</td>
<td>1578.244 (Å(^{3}))</td>
<td>-2.60</td>
<td>20.40</td>
</tr>
</tbody>
</table>

Table 2.3. Percent error in unit cell lattice dimensions of full optimizations with various functionals and basis sets compared to X-ray diffraction.
Having narrowed down to a functional and basis set, the next step consisted of improving the mathematical accuracy of the model through the reduction of the approximations made during the calculations. Improvements included applying a larger grid size for integration of the exchange and correlation energy densities with the program keyword \texttt{XXLGRID}, computing all bielectronic integrals exactly with the program keyword \texttt{NOBIPOLA}, and doubling the number of points used in the numerical derivatives used to calculate vibrational frequencies with the program keyword \texttt{NUMDERIV=2}.

These program keywords were not used earlier in this analysis because of the computational cost. For example, using both keywords during the optimization of CAM-B3LYP/DEF2-SVP increased the computational time by 18%. Applying \texttt{NUMDERIV=2} to the frequency calculation of CAM-B3LYP/DEF2-SVP increased the computational time by 100%.
In this case, the greater accuracy of the optimization calculation using the two applicable keywords did not significantly reduce the error in the lattice dimensions, when compared to the X-ray structure. The lattice dimensions from the improved simulation had an \( \alpha \)-axis error of \(-2.32\%\), \( b \)-axis error of \(-1.27\%\), and \( c \)-axis error of \(1.01\%\). The simulated spectrum resulting from the frequency calculation using all three keywords did show an improvement near 140 cm\(^{-1}\), but few changes in the rest of the spectrum (Figure 2.9).

![Figure 2.9](image.png)

**Figure 2.9.** Frequency simulation results for NQ using CAM-B3LYP/DEF2-SVP and XXLGRID, NOBIPOLA, and NUMDERIV 2 (purple) plotted against the CAM-B3LYP/DEF2-SVP spectrum from Figure 8 (green) and experimental spectrum (blue).
The use of the more accurate theory may have been promising for improving the spectrum near 140 cm$^{-1}$, but the peak near 70 cm$^{-1}$ did not match between experiment and theory as well as the other peaks. It was still shifted to a lower frequency while the other simulated peaks were shifted to higher frequencies. The same observation was present in Figure 2.8, so the application of the more stringent theory did not address the problem. However, this issue was not present in Figure 6 when the optimizations were calculated with a fixed lattice, so we looked more closely at the simulated structure from the calculation with fewer approximations. In both this calculation and the calculations in Figure 2.8, the unit cell volume constricted and the $a$ and $b$ axes both decreased in the optimized unit cell when compared to the experimental dimensions (Table 2.3).

To test how much of an impact the constricted unit cell had on the simulated spectrum, a fixed lattice optimization and the subsequent frequency calculation were completed using CAM-B3LYP/DEF2-SVP with all three program keywords (Figure 2.10).
The fixed lattice simulation provided some interesting insight. Keeping the lattice dimensions fixed during the calculations did improve the placement of the peak near 70 cm\(^{-1}\) by shifting it rather considerably. Fixing the lattice also affected the peaks between 90 cm\(^{-1}\) and 110 cm\(^{-1}\). Figures 2.6 and 2.8 also show the changes in those same peaks when going from a fixed lattice calculation to a full optimization. Initially these changes were considered a by-product of the theory not being complete enough. However, Figure 2.10 suggests instead that these changes can be attributed to the changing lattice dimensions during a full optimization calculation. Therefore, while applying more accurate calculations did improve the simulated spectrum overall, getting the lattice dimensions correct in the simulated structure has proven to be vitally important in accurately modeling crystalline NQ and reproducing its vibrational spectrum.
2.4.3 Structure Analysis

The structure from the fixed lattice optimization of NQ using CAM-B3LYP/DEF2-SVP (with the improved accuracy keywords) was compared against the X-ray measurements. Both the X-ray structure and the simulated structure were visualized, and bond properties were measured, using the Mercury application (v. 3.8) [34]. Comparisons include covalent bond lengths (Table 2.5), covalent bond angles (Table 2.6), and covalent bond torsions (Table 2.7) of NQ.

Table 2.5. Simulated NQ covalent bond distances compared to X-ray measurements.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Experiment</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3-O1</td>
<td>1.252</td>
<td>1.249</td>
</tr>
<tr>
<td>N3-O2</td>
<td>1.240</td>
<td>1.232</td>
</tr>
<tr>
<td>N2-N3</td>
<td>1.337</td>
<td>1.331</td>
</tr>
<tr>
<td>C1-N2</td>
<td>1.373</td>
<td>1.374</td>
</tr>
<tr>
<td>C1-N1</td>
<td>1.316</td>
<td>1.335</td>
</tr>
<tr>
<td>C1-N4</td>
<td>1.326</td>
<td>1.34</td>
</tr>
</tbody>
</table>

**Overall RMSD = 0.011**

Table 2.6. Simulated NQ covalent bond angles compared to X-ray measurements.

<table>
<thead>
<tr>
<th>Angle</th>
<th>Experiment</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-N3-O2</td>
<td>120.33</td>
<td>119.6</td>
</tr>
<tr>
<td>O1-N3-N2</td>
<td>124.35</td>
<td>123.78</td>
</tr>
<tr>
<td>O2-N3-N2</td>
<td>115.32</td>
<td>116.61</td>
</tr>
<tr>
<td>N3-N2-C1</td>
<td>118.88</td>
<td>121.4</td>
</tr>
<tr>
<td>N2-C1-N1</td>
<td>128.22</td>
<td>126.59</td>
</tr>
<tr>
<td>N2-C1-N4</td>
<td>112.46</td>
<td>113.95</td>
</tr>
<tr>
<td>N1-C1-N4</td>
<td>119.31</td>
<td>119.45</td>
</tr>
</tbody>
</table>

**Overall RMSD = 1.402**
Table 2.7. Simulated NQ covalent bond torsions compared to X-ray measurements.

<table>
<thead>
<tr>
<th>Torsion</th>
<th>Experiment</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-N3-N2-C1</td>
<td>2.41</td>
<td>3.38</td>
</tr>
<tr>
<td>O2-N3-N2-C1</td>
<td>-178.23</td>
<td>-177.62</td>
</tr>
<tr>
<td>N3-N2-C1-N1</td>
<td>3.09</td>
<td>4.44</td>
</tr>
<tr>
<td>N3-N2-C1-N4</td>
<td>-177.54</td>
<td>-176.6</td>
</tr>
</tbody>
</table>

Overall RMSD = 1.002

2.4.4 Assignment of Terahertz Spectral Features

The peaks in the experimental spectrum were assigned modes by visual comparison with the corresponding peaks in the simulated spectrum. Vibrational modes in the simulated spectrum were visualized by the Jmol application [35]. Modes were animated one at a time within the application and characterized by the observed motions (Table 2.8).

Table 2.8. Vibrational character of the sub-200 cm\(^{-1}\) IR-active modes in NQ using CAM-B3LYP/DEF2-SVP.

<table>
<thead>
<tr>
<th>Experimental Freq. (cm(^{-1}))</th>
<th>Simulated Freq. (cm(^{-1}))</th>
<th>Mode Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.1</td>
<td>50.2</td>
<td>Rotation about C1-N1 bond</td>
</tr>
<tr>
<td>50.4</td>
<td>54.4</td>
<td>Shear along b-axis</td>
</tr>
<tr>
<td>70.2</td>
<td>72.2</td>
<td>Seesaw about N2</td>
</tr>
<tr>
<td>86.4</td>
<td>93.2</td>
<td>Rocking of whole molecule</td>
</tr>
<tr>
<td>97.2</td>
<td>103.6</td>
<td>Shear along a-axis</td>
</tr>
<tr>
<td>100.7</td>
<td>106.2</td>
<td>Waving (in phase)</td>
</tr>
<tr>
<td>124.1</td>
<td>133.0</td>
<td>Twist around C1-N2 bond</td>
</tr>
<tr>
<td>134.0</td>
<td>142.7</td>
<td>Waving (out of phase)</td>
</tr>
<tr>
<td>154.7</td>
<td>158.9</td>
<td>Twist around N2-N3 bond</td>
</tr>
</tbody>
</table>
2.5 Future Work

A future direction in the work includes finding the theory that does a better job of accurately reproducing the lattice dimensions of the NQ unit cell, ideally resulting in a better simulated spectrum. Improving the theory used for simulating the THz spectrum of NQ is important because that same theory can be used to simulate the Raman spectrum of NQ within CRYSTAL as well. While THz simulations were the focus in this work, a Raman simulation was also conducted using CAM-B3LYP/DEF2-SVP (Figure 2.11) to see how the “winning” combination correlated with the observed Raman spectrum of NQ.

Figure 2.11. Raman experimental spectrum of NQ (blue) plotted against the simulation results for CAM-B3LYP/DEF2-SVP (black) convolved using a Lorentzian line shape with a bandwidth of 1 cm$^{-1}$.

A second direction to consider is using different computational approaches. Other members in this group have used molecular dynamics and anharmonicity calculations within their work to analyze difficult systems. These alternative calculations could also provide insight for this work as to why the SS-DFT simulations are struggling with modeling the unit cell of NQ.
2.6 References


tAL*. Wiley Interdisciplinary Reviews: Computational Molecular Science. 0(0): p. e1360.
CHAPTER 3: Future Direction (Gunshot Residues)

3.1 Introduction

The success of low-frequency vibrational spectroscopy and solid-state density functional theory (DFT) on the analysis of NQ in Chapter 2 implied that such techniques would also be successful in characterizing similar compounds. In deciding on what compounds to investigate next, we re-visited NQ’s role and found its action as a propellant applies not only to explosives, but also to firearms as it is present in certain types of gunpowder. This lead to the idea of analyzing other organic compounds present after a firearm is discharged, compounds known as gunshot residues (GSR).

Gunshot residues are the molecular compounds that result after gunpowder reacts during the discharge of a firearm. The development of analytical techniques for investigating these gunshot residues is a popular topic in recent years as shown by the several recent reviews on the subject [1-4]. Analyzing these residues is important in the field of forensic science and criminal investigations trying to connect a suspect with a crime scene. For example, if a firearm was discharged at the scene of a crime, the GSR from that discharge would be found on the gun itself, on the skin and clothes of the person who used the gun, and on anyone standing within 3 ft of the shooter [5].

The applicability of Raman and IR spectroscopy in analyzing GSR have clearly been shown in the literature either independently [2, 6-12], or used in conjunction with each other [13]. These non-destructive and non-invasive techniques can identify the presence of GSR when compared against known spectra using spectral “fingerprints” of the different residues.
However, very little spectral data has been published in the low-frequency region as literature focuses on the mid to near IR range.

In this work, low-frequency Raman and THz spectroscopies were used to find the low-frequency spectral fingerprints of three GSR’s, ethyl centralite, 2-nitrodiphenylamine, and 1,3-diphenylurea, to provide and characterize vibrational data in a spectral range not yet published. Follow-up work includes using solid-state density functional theory to model the three GSR’s and assign specific vibrational modes to the features of the collected spectra.

3.2 Methods

The following chemicals (listed in Table 3.1) were ordered from Sigma-Aldrich (St. Louis, MO), 1,3-diethyl-1,3-diphenylurea also known as ethyl centralite (EC), 2-nitrodiphenylamine (2NDPA), and 1,3-diphenylurea (DPU).

<table>
<thead>
<tr>
<th>Residue</th>
<th>CAS Number</th>
<th>Lot Number</th>
<th>Catalog Number</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>85-98-3</td>
<td>05107LF</td>
<td>372889</td>
<td>99%</td>
</tr>
<tr>
<td>2NDPA</td>
<td>119-75-5</td>
<td>0517Jl</td>
<td>157171</td>
<td>98%</td>
</tr>
<tr>
<td>DPU</td>
<td>102-07-8</td>
<td>STBD5926V</td>
<td>142158</td>
<td>98%</td>
</tr>
</tbody>
</table>

3.2.1 THz Sample Preparation and Instrumentation

Pellets for THz spectroscopic measurements were prepared by mixing a small amount of powdered sample (20-30 mg) into a non-absorbing matrix. The amount of sample used in each case was dependent on the absorption strength of the sample. The matrix used for all pellets was polytetrafluoroethylene (PTFE) due to its weak low-frequency absorption in the THz range.
frequency range of interest (below 200 cm\(^{-1}\)). The mixture of sample and matrix was then placed in a stainless-steel vial with a ball bearing and pulverized using a ball mill (Dentsply Rinn 3110-3A) to ensure the sample and matrix were a homogenous mixture. Approximately 550 mg of the resulting mixture was then pressed into a pellet using a hydraulic press (ICL EZ-Press 12) with a steel die at a pressure of 2000 psi. This process was repeated for each of the three GSR samples as well as for a blank pellet of pure PTFE to create pellets 13 mm in diameter and 2 mm thick.

A cryostat was used to hold the samples and the blank during the THz spectroscopic measurements. This sample chamber was held under vacuum during the collection of the data. The external THz beam path was continuously purged with dry air to prevent any water absorption peaks from appearing in the sample and blank data sets. Spectroscopic measurements for THz were taken at room temperature (290 K) and liquid nitrogen cooled temperature (78 K) through polymethylpentene polyolefin resin (TPX) windows on the cryostat.

A Menlo Systems TERA K15 Time-Domain THz Spectrometer (Martinsried, Germany) was used to capture sample and blank waveform data. The data was then truncated to remove reflections from the pellet and averaged over 3 separate waveform scans, resulting in a data range of 14 ps from the pulse to the cut-off. The spectra resolution for this truncated data was 2.38 cm\(^{-1}\). The laser source is a 1.5 µm femtosecond fiber laser with InGaAs photoconductive antennas for THz generation and detection. The observed bandwidth was 0.3 - 3.9 THz (10 -130 cm\(^{-1}\)).
3.2.2 Raman Sample Preparation and Instrumentation

Pellets for Raman spectroscopic measurements were made of pure sample. ~300 mg of each sample was pressed using the hydraulic press at a pressure of 2000 psi.

An ONDAX (Monrovia, California) low-frequency THz-Raman XLF-CLM laser with excitation wavelength 784.7 nm and fiber-coupled to an ANDOR Shamrock SR-750 spectrometer with a CCD iDus camera was used for data collection. The system spectral resolution of this system set-up is 0.6 cm\(^{-1}\).

A cryostat was used to hold the samples and the blank during the Raman spectroscopy. This sample chamber was held under vacuum during the collection of the data. Spectroscopic measurements for Raman were taken at room temperature (290 K) and liquid nitrogen cooled temperature (78 K) using 225 acquisitions at 3 second exposure times through glass windows on the cryostat.

3.2.3 Theoretical Methods

Solid-state density functional theory (SS-DFT) calculations utilizing periodic boundary conditions were performed with the CRYSTAL17 software package [14]. Only a single functional and basis set combination was used to model each GSR. The combination of the functional PBE [15] with the Ahlrichs VTZ with polarization (VTZp) [16] basis set (PBE/VTZp) was used as the initial theory to simulate the low-frequency THz vibrational spectra.
3.3 Results/Spectra

The experimental Raman and THz spectra for the three GSR’s are shown in the following figures. Regardless of what the spectra held, acquiring the low-frequency spectra of the GSR’s was interesting because no low-frequency work has been done with them that we could find in the literature. We weren’t sure what we were going to find, if we were going to find anything.

3.3.1 Ethyl Centralite

Ethyl centralite, or 1,3-diethyl-1,3-diphenylurea, is present in double base gun propellants as a stabilizer. It has a monoclinic unit cell (Figure 3.1) and the crystal structure [17], published in the Cambridge Structural Database (CSD) [18], was used as the intitial coordinates for the SS-DFT simulations.

![Figure 3.1](image)

**Figure 3.1.** Ethyl centralite molecule (left) and the unit cell of crystalline ethyl centralite (right). Atoms are colored as follows: oxygen (red), nitrogen (blue), carbon (gray), and hydrogen (white).
The THz spectra (Figure 3.2) and Raman spectra (Figure 3.3) of EC showed that there were, in fact, low-frequency peaks present in both cases. Therefore, a simulation using PBE/VTZp was started to begin the computational analysis for this system. The initial THz spectrum simulation is shown in Figure 3.4.

**Figure 3.2.** THz experimental spectra of EC at 290 K (red) and 78 K (blue) with a 549.9 mg pellet at 4.0% concentration by mass.
Figure 3.3. Raman spectra for EC at 290K (red) and 78K (blue) with a 308.2 mg pellet, normalized to one.

Figure 3.4. THz experimental spectrum of EC at 78 K (blue) and calculated spectra (black) using PBE/VTZp convolved using a Lorentzian line shape with a bandwidth of 3 cm$^{-1}$. 
3.3.2: 2-Nitrodiophenylamine

2-Nitrodiophenylamine, also called \(N\)-phenyl-2-nitroaniline or \(N\)-(2-nitrophenyl)phenylamine), is also present in double base gun propellants as a stabilizer. It also has a monoclinic unit cell (Figure 3.5) and the crystal structure [19] from the CSD was used as the initial coordinates for the SS-DFT simulations.

![Figure 3.5](image)

*Figure 3.5. 2-Nitrodiophenylamine molecule (left) and the unit cell of crystalline 2-nitrodiophenylamine (right). Atoms are colored as follows: oxygen (red), nitrogen (blue), carbon (gray), and hydrogen (white).*
The THz spectra of 2NDPA (Figure 3.6) showed several well-resolved low-frequency features. The Raman spectra (Figure 3.7) of 2NDPA, on the other hand, had little observable features due to the high baseline caused by fluorescence. A simulation for 2NDPA using PBE/VTZp was conducted to start the investigation of the THz features. The initial THz spectrum simulation is shown in Figure 3.8.

![THz Spectra](image.png)

**Figure 3.6.** THz experimental spectra at 290 K (red) and 78 K (blue) for 2NDPA with a 562.7 mg pellet at 3.8% concentration by mass.
Figure 3.7. Raman spectra at 290K (red) and 78K (blue) for 2NDPA with a 301.1 mg pellet.

Figure 3.8. THz experimental spectra for 2NDPA at 78 K (blue) and calculated spectrum (black) using PBE/VTZp convolved using a Lorentzian line shape with a bandwidth of 3 cm$^{-1}$. 
3.3.3: 1,3-Diphenylurea

1,3-Diphenylurea, also called carbanilide or $N,N'$-diphenylurea, has a monoclinic unit cell (Figure 3.9) and the crystal structure [20] was chosen as the source of the initial coordinates for the SS-DFT simulations from the several published structures on the CSD. This particular structure was solved at the lowest temperature (100 K) and calculations in CRYSTAL are conducted using a zero temperature approach [14], therefore using a crystal structure at the lowest available temperature was preferred.

**Figure 3.9.** 1,3-Diphenylurea molecule (left) and the unit cell of crystalline 1,3-diphenylurea (right). Atoms are colored as follows: oxygen (red), nitrogen (blue), carbon (gray), and hydrogen (white).
Both the THz spectra (Figure 3.10) and Raman spectra (Figure 3.11) of DPU showed several features. A simulation for DPU using PBE/VTZp was conducted and the initial THz spectrum simulation is shown in Figure 3.12.

**Figure 3.10.** THz spectra of DPU at 290 K (red) and 78 K (blue) with a 554.2 mg pellet at 4.0% concentration by mass.

**Figure 3.11.** Raman spectra of DPU at 290K (red) and 78K (blue) with a 382.6 mg pellet.
3.4 Conclusion and Future Work

Pursuing the low-frequency spectra of the three GSR’s discussed in this work proved worthwhile as most spectra showed prominent features. The computational analysis on these residues will be continued to find the best theory to accurately model these systems. Once the structures and spectra (both THz and Raman) are accurately simulated, the investigation of these GSR’s can continue with the assignment of vibrational modes. Characterizing this unexplored region of bandwidth for these residues will improve the spectral fingerprint database available for forensic investigations.

Figure 3.12. THz experimental spectra for DPU at 78 K (blue) and calculated spectrum (black) using PBE/VTZp convolved using a Lorentzian line shape with a bandwidth of 3 cm\(^{-1}\).
3.5 References

APPENDIX A: Waveform Processing Program

THz waveform processing program written by Rebecca Prendergast, with the assistance of Prof. John Franck, at Syracuse University.

What goes in: your THz data in an excel sheet (see below for specific requirements)
What comes out: Plots to give you a snapshot of data quality and a text file with transformed/zero-padded ratio data.

To use this script, your waveform data needs to be in an excel file with three columns.
1st - wavenumbers
2nd - Blank singal (labeled "Blank")
3rd - Sample signal (labels "Sample")

You need a separate excel file for each sample since this script can only process one file (with one tab) at a time.

To use this script, you will need the following installed:
- Python 2.7
- Tkinter (should come with python)
- Pandas (for reading different files types, should come with Python)
- pyspecdata (Prof. John Franck's python library for spectra analysis, run pip install pyspecdata)

Calls up a search window to input the data and asks for input about the molecule and calc specs''

from Tkinter import Tk
from tkFileDialog import askopenfilename
Tk().withdraw()
datafile = askopenfilename()
print datafile

molecule = raw_input("Molecule: ")
molecule = str(molecule)
molecule = str.strip(molecule)
print "\n"

blackman_range = raw_input("What size Blackman Window do you want to use? \n(usual is +/-15): +/-")
blackman_range_1 = str.strip(blackman_range)
blackman_range_2 = float(blackman_range)
print "\n"

zero_padding = raw_input("How many points do you want to use for zero-padding? \n(must be a power of 2, usual is 16384): ")
zero_padding_1 = str.strip(zero_padding)
zero_padding_2 = int(zero_padding)
print "\n"

'''code to transform, zeropad, and plot the THz spectra'''
from pyspecdata import *
import pandas as pd
#import math as m
import os
fl = figlist_var()

# importing the excel file
data = pd.read_excel(os.path.expanduser(datafile))

# huge loop analyzing the data and creating figures to show it
with figlist_var(filename= molecule +'THz') as fl:
    alldata = {}
    for j,thiscol in enumerate(data.columns):
        thisname = thiscol.encode('ascii').strip()
        # reading the blank data from the excel sheet and assigning it to the time axis
        thisdata_PTFE = nddata(data['Blank'].values,'t_PTFE')
t_axis_PTFE = linspace(data.index.values[0],data.index.values[-1],len(data.index.values))
        thisdata_PTFE.setaxis('t_PTFE', t_axis_PTFE)
t_PTFE_max = abs(thisdata_PTFE).argmax('t_PTFE').data
        thisdata_PTFE.setaxis('t_PTFE', lambda x:x-t_PTFE_max)
        # reading the sample data and assigning it to the time axis
        thisdata_Sample = nddata(data['Sample'].values,'t_Sample')
t_axis_Sample = linspace(data.index.values[0],data.index.values[-1],len(data.index.values))
        thisdata_Sample.setaxis('t_Sample', t_axis_Sample)
t_Sample_max = abs(thisdata_Sample).argmax('t_Sample').data
        thisdata_Sample.setaxis('t_Sample', lambda x:x-t_Sample_max)

        # uncomment the max value you want to use for normalization/what you want ot normalize both spectra to, and comment out the one you don't want to use
        #max_value = th
        #thisdata_PTFE.runcopy(max,'t_PTFE')
        # (or)
        max_value = thisdata_Sample.runcopy(max, 't_Sample')

        # normalizing the data so that it fits under the blackman window
        # (that has a max value of 1)
        normal_PTFE = thisdata_PTFE.copy()
        normalized_PTFE = normal_PTFE / max_value # max value between both waveforms
        normal_Sample = thisdata_Sample.copy()
        normalized_Sample = normal_Sample / max_value # max value between both waveforms
thisdata_PTFE = normalized_PTFE
thisdata_Sample = normalized_Sample

# prints the max value after normalization to check yourself (both should be 1 or less than 1), if they aren't you have to swap your max value definition
print thisdata_PTFE.runcopy(max, 't_PTFE')
print thisdata_Sample.runcopy(max, 't_Sample')

### Note to myself: add an error or something if one of the maxes are greater than 1, because then the max value calc needs to swap and they'll have to re-run the script

fl.next('Time Domain') # plots the waveform and the blackman filter that is applied
if j==0:
    b_PTFE = thisdata_PTFE.copy()
    b_PTFE['t_PTFE':(-blackman_range_2,blackman_range_2)] = blackman(len(thisdata_PTFE['t_PTFE':(-blackman_range_2,blackman_range_2)].data))
    b_Sample = thisdata_Sample.copy()
    b_Sample['t_Sample':(-blackman_range_2,blackman_range_2)] = blackman(len(thisdata_Sample['t_Sample':(-blackman_range_2,blackman_range_2)].data))
    fl.plot(b_PTFE, alpha = 0.5, label = 'blackman PTFE')
    fl.plot(b_Sample, alpha = 0.5, label = 'blackman Sample')
    fl.plot(thisdata_PTFE, alpha = 0.5, label = 'PTFE')
    fl.plot(thisdata_Sample, alpha = 0.5, label = 'Sample')

fl.next('Frequency Domain') # plots the data in the frequency domain
thisdata_PTFE *= b_PTFE
thisdata_PTFE.ft('t_PTFE', shift = True, pad = zero_padding_2)
thisdata_Sample *= b_Sample
thisdata_Sample.ft('t_Sample', shift = True, pad = zero_padding_2)
fl.plot(abs(thisdata_PTFE)['t_PTFE':(0,4)], alpha = 0.5, label = "angle: PTFE")
fl.plot(abs(thisdata_Sample)['t_Sample':(0,4)], alpha = 0.5, label = "angle: Sample")
alldata['PTFE'] = thisdata_PTFE
alldata['Sample'] = thisdata_Sample

fl.next('Ratio') # the plot we use/publish
print alldata.keys()
ratio_data = alldata['PTFE'].copy()
ratio_data.data =
log10(abs(alldata['PTFE'].data)/abs(alldata['Sample'].data)) * 2
fl.plot(abs(ratio_data)['t_PTFE':(0.24,4.5)], alpha = 0.5)

""" writing the ratio data to a text file so you can plot it in Origin"""
temp_file = open(molecule + '_ratio_data.txt','w')
temp_file.write("Ratio data of " + molecule + "\n" + "(with blackman window range +/-" + blackman_range_1 + " and " + zero_padding_1 + " points after zero-padding)"
)temp_file.write("\n")temp_file.write("\n")
You have options of what you want in the text file, if you want the signal before and after processing (first option) or if you want just the processed data to plot (second option). Just uncomment/comment out and necessary.
"
#temp_file.write("THz" + "t" + "t" + "Wavenumber" + "t" + "FFT" + 5*"t" + "Magnitude")temp_file.write("Wavenumber" + "t" + "Magnitude")
```
temp_file.write("\n")
i = 0
while i < len(ratio_data.data):
data_string_t = str(ratio_data.getaxis('t_PTFE')[i])data_string_cm = str(33.33 * ratio_data.getaxis('t_PTFE')[i])data_string_FFT = str(ratio_data.data[i])data_string_Mag = str(abs(ratio_data.data[i]))
#same here, comment or uncomment out as necessary (first option for all the data, second option for just the ratio data
#temp_file.write(data_string_t + "t" + data_string_cm + "t" + data_string_FFT + 3*"t" + "t" + data_string_Mag)
temp_file.write(data_string_cm + "t" + data_string_Mag)
temp_file.write("\n")i = i + 1
temp_file.close()"
APPENDIX B: Spectrograph Calibration Procedures

Based on the Shamrock Wavelength Calibration procedures under Andor Technology’s Technical Solutions

- **Issue:**
  - Rayleigh peak was off-center (not at zero wavenumbers). Peak positions were not where they were expected when compared against the standards taken at time of installation.

- **Possible Cause:**
  - Changes in temperature/conditions within the lab from different seasons. The instrument was installed in June, while initial issues were noticed in November.

- **Correction:**
  - Re-calibrate the detector to the reference lamp (Mercury-Neon Emission PEN-RAY Lamp).
  - Recommend calibrating the spectrometer every 6 months to account for seasonal changes.

What you will need is shown in Figure A.1:

![Figure A.1](image)

**Figure A.1.** Equipment needed (from left to right): lamp plate, slit input plate, 4 screws, the hex key wrench, Mercury-Neon pen-ray lamp, lamp power source
**Calibration Step 1**: Setting-up the Slit Input and Reference Lamp

1) Make sure the spectrograph is turned off, the laser is turned off, and you have exited the SOLIS software on the computer
2) Remove the fiber input plate from the back of the spectrograph (be careful not to kink the fiber input cord as you remove the plate)
3) Mount the slit input plate to the same place on the back of the spectrograph (Figure A.2)

![Figure A.2. Proper mounting of slit plate](image)

4) Set the slit width to 10 μm using the knob on the slit input plate (Figure A.3)

![Figure A.3. Slit width set to 10 μm](image)
5) Mount the lamp plate onto the slit input plate (side with the pinprick hole facing in to the spectrometer) (Figure A.4 and Figure A.5)

![Figure A.4. Lamp plate (side that will face in)](image)

![Figure A.5. Proper mounting of the plate](image)

6) Insert the lamp, connect it to the power source, and plug in the power source (do not turn the lamp on until it is properly inserted as shown in Figure A.6)

![Figure A.6. Final set up of slit input with lamp](image)

7) Turn on the spectrograph
8) Turn on the lamp
9) Load the SOLIS software
10) You are now ready to calibrate the detector.
Calibration Step 2: Procedures Using the Slit Plate/Calibrating the Detector

1) On the software display, ensure the “Offset Adjustment” control is shown in the bottom right-hand corner of the screen. If it’s not showing, click on the “Display” on the bottom left-hand side and check Offset Adjustment. Or re-load the configuration file (because the correct file should have this displayed upon loading the software). The correct configuration file you should have loaded is `AndorSolis-06202017.cfg` last modified 6/20/2017 at 12:35 PM (the original file from the instrument installation, Under File->Configuration Files -> Load...)

2) On the offset adjustment control, click the “Detector” tab if not already selected.

3) If “Grating 2” is not selected, click on the red side of the triangle under “Grating” to set it there. We only use this setting and will calibrate/re-calibrate this grating.

4) If the shutter is not set to “AUTO”, click on it until it is.

5) Change the x-axis label from wavenumbers to wavelength (Under Calibrate -> Change Units -> Use the drop-down menu to select Wavelength -> Click “Calibrate” -> Close the window)

6) Set the center wavelength to 703.24 nm. (Note: We choose this wavelength because our laser is 784.7 nm and the closest and strongest peak is 703.24 nm as recommended by the Shamrock Wavelength Calibration document.)

7) Double check that the bottom left box has changed from red to blue and is at -70°C.

8) Your screen should now look like Figure A.7.

9) Acquire data (single acquisition), set the view to “2D with peak labels”, and click “99:1”
10) If a red vertical line at the center of the acquired spectra is not shown, turn it on by clicking the little box with a picture of a spectra and line in the “Offset” box (bottom right). This will make adjusting the grating offset much easier with the red line (assigned to the center wavelength) to compare to the acquired spectra.

11) If the red line does not align with the 703.24 peak, then you need to adjust the offset to make the two line up/match. Make sure to zoom in to get a better comparison if needed as shown in Figure A.8.

![Figure A.8. Example of the center wavelength offset from the signal wavelength](image)

12) Acquire data with the “video” button to get constant updates to the spectra as you adjust the detector offset.

13) Press the + or – on the detector offset (bottom right) as needed to line up the center (red) line with the appropriate peak. You can change the value of the +/- by right clicking on the buttons (i.e. +/-1, +/-100, etc.). Proper alignment is shown in Figure 9.

![Figure A.9. Example of center wavelength properly aligned to reference signal](image)
14) Once they’re aligned, we’re finished with the offset adjustment portion. The offset you entered will be saved automatically and will load when you load the software next. (But write it down just in case!)

**Calibration Step 3: Procedures Refining the Fiber Input Placement/Calibrating Rayleigh Peak**

1) Turn off the spectrograph and the lamp and close out of the SOLIS software.
2) Remove the lamp (make sure it’s turned off first!)
3) Remove the lamp plate and the slit plate.
4) Mount the fiber input plate as shown in Figure A.10 (be careful of the fiber cord)

![Figure A.10. Proper mounting of the fiber input](image)

5) Turn the spectrograph back on, boot up the SOLIS software, and turn on the laser.
6) Check that everything is set-up in the software like it was in Calibration Step 2 (parts 1-5). The offset value shown should be the number you entered at the end of the previous calibration section.
7) Change the x-axis units to wavelength (Under Calibrate -> Change Units -> Use the drop-down menu to select Wavelength -> Click “Calibrate” -> Close the window)
8) Set the center wavelength as the laser wavelength (784.67 nm in our case) and turn on the red center line.
9) Double check that the bottom left box has changed from red to blue and is at -70°C.
10) Insert a sample to be tested for the software calibration. You can use any sample as a test because we are only looking at the Rayleigh peak.
11) Acquire data using the video button (which will give constant updates to the spectra) and change view to “2D”.
12) If the Rayleigh peak isn’t centered on the red line (shown in Figure A.11), use the horizontal knob on the fiber input mount (x-axis adjustment) and turn it slightly either way as needed until the Rayleigh peak lines up with the center line (Figure A.12). Zoom in as needed to be more accurate.

Figure A.11. Example of an offset of the Rayleigh peak

Figure A.12. Proper horizontal alignment of the Rayleigh peak

13) To check the y-axis, zoom back out and take a single acquisition. Change the display to “image”. The horizontal line of black should be centered in the middle of the white background and a white signal is visible at the center wavelength as shown in Figure A.13 (shouldn’t need any adjusting).
14) If it does need adjusting, take acquisitions with “video” and use the vertical knob to adjust the y-axis of the fiber input (like what you did with the x-axis/Rayleigh peak).

![Figure A.13. Proper vertical alignment of the data](image)

15) Change the x-axis back to Raman shift and change the view to “2D” to double check everything looks ok and the Rayleigh peak is at zero (Under Calibrate -> Change Units -> Use the drop-down menu to select Raman shift -> Click “Calibrate” -> Close the window)

The calibration is now complete.
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**Education**

| BS | U.S. Coast Guard Academy, Marine and Environmental Sciences | May 2012 |

**Honors and Awards**

**U.S. Coast Guard Awards**
- Coast Guard Achievement Medal
- Unit Commendation Medal
- Meritorious Unit Commendation
- Meritorious Team Commendation
- Coast Guard “E” Ribbon
- Arctic Service Medal (3)
- National Defense Service Medal
- Sea Service Ribbon

2008-present

**Research Experience**

**Syracuse University**, Syracuse, NY  
Graduate Student, Advisor: Prof. Timothy Korter  
- Combined terahertz time-domain spectroscopy and THz-Raman spectroscopy and solid-state density functional theory (DFT) to study vibrational modes of small crystalline organics.
- Investigated the relationship between elasticity and impact sensitivities of high energy materials in the nitroaromatics family through solid-state DFT simulations.
- Developed custom software for processing terahertz waveforms to include zero-padding, filtering, and Fourier transforming the waveform into the frequency-domain.

2016 to 2018

**U.S. Coast Guard Academy**, New London, CT  
Undergraduate, Advisor: Prof. Joshua Gray

2011 to 2012

**Laboratory Skills**

**Experimental Techniques**
- Terahertz Spectroscopy
- Raman Spectroscopy
**TEACHING EXPERIENCE**

**Syracuse University**, Syracuse, NY  
**Teaching Assistant/Tutor volunteer**, Chemistry Department  
Aug 2017 to May 2018

- Volunteered as a tutor, assisted the instructors with preparing and administering exams, scheduled appointments with students to review lecture concepts and assist with homework, held exam review sessions.

**U.S. Coast Guard Academy**, New London, CT  
**Certified Peer Tutor**  
Aug 2009 to Jan 2011

- Participated in the peer tutor program, acted as the equivalent of a Teaching Assistant at a civilian college, attended trainings for teaching strategies, scheduled appointments with students, hosted study sessions.

**PUBLICATIONS**

Gray, J. P., Burgos, D., Yuan, T., Seeram, N., Rebar, R., **Follmer, R.**, Heart, E.  

**PRESENTATIONS**


**PROFESSIONAL TRAINING**

**Workshops**  
BRUKER APEX II Duo Service Training, Syracuse, NY, August 8-10th, 2017  
Ab initio Modeling in Solid State Chemistry, Minneapolis, MN, July 9-14th, 2017

**Certification**  

**USCGC MACKINAW (WLBB 30)**, Assistant Operations Officer, Operations Department, July 2014-July 2016

- Assistant Operations Officer - Supervised 14 department personnel and oversaw execution of departmental responsibilities. Planned and scheduled missions and logistics for ship operations ranging across all five Great Lakes.
- Navigator Qualification - Responsible for creating track-lines and ensuring safe navigation.
• Officer of the Deck Qualification - Responsible for the safety, navigation, and ship’s mission performance as a vessel operator.

**USCGC HEALY (WAGB 20)**, Marine Science Officer, Operations Department, June 2012-July 2014
• Officer of the Deck Qualification - Responsible for the safety, navigation, and performance of the ship’s missions as a vessel operator.
• Marine Science Officer - Served as the science researchers’ liaison onboard.

**PROFESSIONAL AFFILIATIONS**

American Chemical Society (ACS), 2017-Present
United States Coast Guard, 2008-Present

**COMMUNITY SERVICE**

**U.S. Army**
Family Readiness Group Leader, Fort Drum, NY, May 2017-June 2018

**U.S. Coast Guard**
Victim Advocate, USCGC MACKINAW, Cheboygan, MI, August 2014-June 2016

**U.S. Coast Guard**
Victim Advocate, USCGC HEALY, Seattle, WA, January 2013-June 2014

**LANGUAGES**

**English:** Native Language

**COMPUTER SKILLS**

**Programming:** Python 2.7

**Applications:** Microsoft (Word, Excel, PowerPoint), Origin 2017, Mercury (CSD)