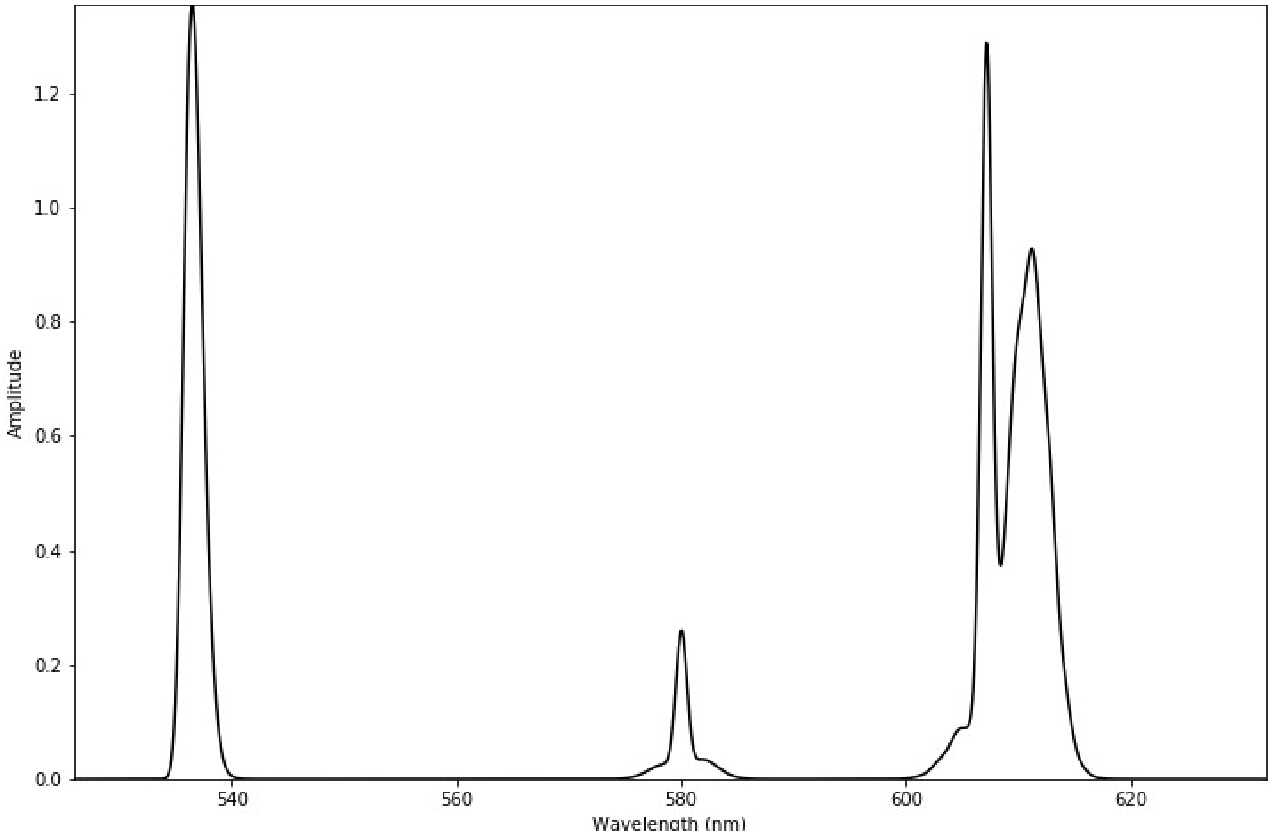


Technical theory behind my Python3 Raman spectroscopy simulation program

Eric Anthony Comstock

May, 2021

TEXAS A&M UNIVERSITY
1876

Introduction

In the 2020-2021 academic year, I participated in a project at Texas A&M University to use Raman spectroscopy to do diagnostics on hypersonic flames, as part of the process of the development of commercial scramjets. At present, most commercial flight is subsonic or transonic, which only allows for maximum velocities in the regime of 250 meters per second in cruise. As the Earth has a circumference of roughly 40,000 kilometers, though, a hypothetical flight between antipodes would take approximately 80,000 seconds, or a bit more than 22 hours. Under these conditions, it is not possible to have the capability to be anywhere in the world in a single day, and some trips can take two or more days once multiple flights, luggage, security, and various bureaucracies are accounted for.

Using scramjets instead of turbojets, however, would allow for a much faster form of flight, in the hypersonic regime of above five times the speed of sound. For example, at six times the speed of sound, velocities would be in the range of 2 kilometers per second, with would allow a flight between antipodes in just three hours. This would allow anyone to go anywhere, on extremely short notice, in a single day – which would be a huge boon to international corporations that must manage disparate overseas subsidiaries, for example. This excited me because of both the scientific and the economic potential of this technology.

To develop these scramjets, though, the chemistry of combustion in hypersonic flows, and the engineering needed to extract useful work from this combustion, must be characterized. Diagnostics of hypersonic flames can be used to analyze the chemical reactions involved, and to help the characterization of the system. To help with this project, I developed a program using Python3 to generate Raman spectra for arbitrary mixtures of gases at arbitrary temperatures, given sufficient input data. This was done by simulating the quantum dynamical properties of simplified molecular systems with regards to both rotational and vibrational motion. After the program was used to generate spectra, the spectra could be compared to experimental results. These comparisons could be used to find the concentrations and temperatures of different gases at different locations in the flame.

Overview

Rovibrational Raman spectroscopy is based on the observation of rotational and vibrational transitions of molecules in a sample of a given substance. Rotational transitions occur during a change in the quantum rotational energy state of a molecule, and vibrational transitions occur during a change in the quantum vibrational energy state of a molecule. First, the rotational aspect of Raman spectroscopy will be discussed.

Rotational spectroscopy

The energies of the rotational states of most molecules can be described by the rigid-rotor model, which is a quantum model that assumes that the molecule is completely rigid and capable of rotation (hence rigid-rotor). It should be noted that this only applies to diatomic molecules, and more advanced methods are required for molecules with more than two atoms, such as carbon dioxide, or water. However, examining the transitions for diatomic molecules provide insight into the behavior of molecules of higher complexity. Applying the Schrodinger Equation, the energy levels of such a molecule are found to be $E = J(J+1)h^2/8\pi^2I$, where I is the moment of inertia of the molecule, determined by summing the angular inertia of every atom in the molecule with respect to the axis of rotation in question, h is Planck's constant, and J is the quantum number of the energy level. $h^2/8\pi^2I$ is customarily denoted B, making the energy of a rotational state $E = J(J+1)B$.

Using this equation, the rotational transitions between J = n and J = n+2 can be found to have an energy difference of (4n+6)B. Thus, a transition from J = 0 to J = 2 gains 4B of energy, and a transition from J = 102 to J = 100 releases 406B of energy. This equation will be shown to be important later.

Rotational transitions can be measured using Raman spectroscopy, where a monochromatic laser is fired into a sample, exciting it to a high energy level, leading to scattering. While in most instances this scattering is elastic, where the photon leaves with the same amount of energy it entered with, the scattering will sometimes be inelastic, where the energy of the photon changes while it is being scattered, also changing the energy of the material, usually altering its rotational or vibrational quantum state. This inelastic scattering is known as Raman scattering, while elastic scattering is known as Rayleigh scattering. When the final rotational state of the material is different than the initial state, the energy difference is transferred to the scattering photon, which shifts frequencies in a detectable manner (This phenomenon is known as Raman scattering.). The difference between the photon energy of the scattered photon and the energy of a photon from the laser can be measured to yield the energy absorbed or released by the sample. This energy difference is known as the Raman shift.

The most common transitions observed with Raman spectroscopy are vibrational and rotational transitions. Let us focus on the rotational aspect of Raman spectroscopy. A peculiar property of quantum rotational states is that only transitions of $\Delta J = \pm 1$ are possible. As the process of Raman spectroscopy includes two changes in the energy of a molecule, the rotational state changes twice, making $\Delta J = 0$ and $\Delta J = \pm 2$ the only possible transitions. When $\Delta J = 0$, the scattered photon is called Rayleigh scattering, and gives no useful information. However, when $\Delta J = \pm 2$, a Raman shift of +(4n+6)B or –(4n+2)B is produced (where n is the level of the original rotation state). Using this method, the initial rotational states and composition of the sample can be measured, as different gases will have different values of B, which can be measured through analysis of the spectrum.

It is worth noting that rotational spectroscopy is only effective on gaseous samples, as liquids and solids prevent free rotation in many cases (F_2 is a notable exception to this, as its molecules can rotate freely inside its solid form's crystal structure.).

At room temperature, there is enough ambient energy in most substances to excite most of the molecules to excited rotational states. The distribution of the molecules in a sample across rotational states can be found by using the Boltzmann factor. The Boltzmann factor is the ratio between the populations of two arbitrary states, and can be calculated as follows: $p_i / p_j = (N_i / N_j)e^{(E_j - E_i)/kT}$, where i and j are the two states, p is the population of the state referenced by its subscript, E is the energy of the state referenced by its subscript, N is the degeneracy of the state referenced by its subscript (N = 2J + 1 for rotational states), T is the temperature of the environment, and k is the Boltzmann constant, 0.695034800 wavenumbers per degree Kelvin. This formula can be used to find the populations of all rotational states in a sample as functions of the ground rotational state.

As the Boltzmann factor reduces in magnitude when the temperature of the sample increases, the temperature of a sample can also be determined from its spectrum. Samples at higher temperatures have wider spectra with more peaks, and samples at a lower temperature have more narrow spectra with fewer peaks.

Another important factor is the conversion from wavenumber space to wavelength space. To convert a small shift in photon energy to a small shift in wavelength, the approximate wavelength of the photon must be known. For example, if the original monochromatic light from the Raman spectrometer was at 532 nanometers, or 18797 wavenumbers, a shift in frequency of 1 wavenumber would lead to a frequency of 18798 wavenumbers, or a wavelength of 531.971 nanometers, corresponding to a shift of 0.029 nanometers. This method can be used to re-enumerate the Raman shift in wavelength space.

Is it also important to note that the amplitude of the spectral peaks with less energy than the laser used (termed Stokes Raman scattering) is greater than the peaks with more energy than the laser used (termed Anti-Stokes Raman scattering), on average. This is because more molecules of the sample will be in lower states than higher states, making jumps up in energy more common than jumps down.

Vibrational spectroscopy

The vibrational aspect of Raman spectroscopy allows for a number of other spectral peaks, at much greater Raman shifts than the purely rotational peaks. The Raman selection rules also allow for vibrational transitions, but only in conjunction with rotational transitions. Thus, for every vibrational transition possible, an entire new spectrum is produced of the molecule in question, displaced by the magnitude of the vibrational transition.

All molecules have vibrational modes, which are where the atoms of a molecule vibrate extremely quickly – a few tens of trillions of times per second, approximately. Not all of these vibrational modes are Raman-active, though – to be active in Raman spectroscopy a vibrational mode must change the polarizability of the molecule. Vibrational transitions can include stretches, rotations, changes in the angle between bonds, or a mixture of all three. However, as the quantum harmonic oscillator model can be easily applied only for diatomic molecules, which have one Raman-active vibrational mode (stretching of the single bond), the following calculation will solely concern them. Molecules with more than two atoms typically require more advanced methods to determine their vibrational modes.

To find the energies of these states and transitions, the quantum harmonic oscillator model will be used to represent the potential energy gradient of the molecular bonds being analyzed, with the point of lowest potential energy being assumed to be the resting state. While this model is grossly inaccurate at high energy levels, due to both the high electrical repulsion between extremely close nuclei, and the possibility of the atoms separating forever at finitely high states of excitation, the model works well for the first few vibrational energy levels, which contain the vast majority of molecules at room temperature. Applying the Schrodinger Equation, the energy levels of such a molecule are found to be $E = (2v + 1)h(k_f/m)^{1/2}/4\pi$, where v is the quantum number of the vibrational energy level, k_f is the spring force, and m is the reduced mass of the system. As these energy levels increase in a linear matter, only one distinct vibrational energy transition per vibrational energy mode can be seen by Raman spectroscopy, apart from the purely rotational spectrum, with the vibrational transition appearing as a replica of the original rotational spectrum of the component in question.

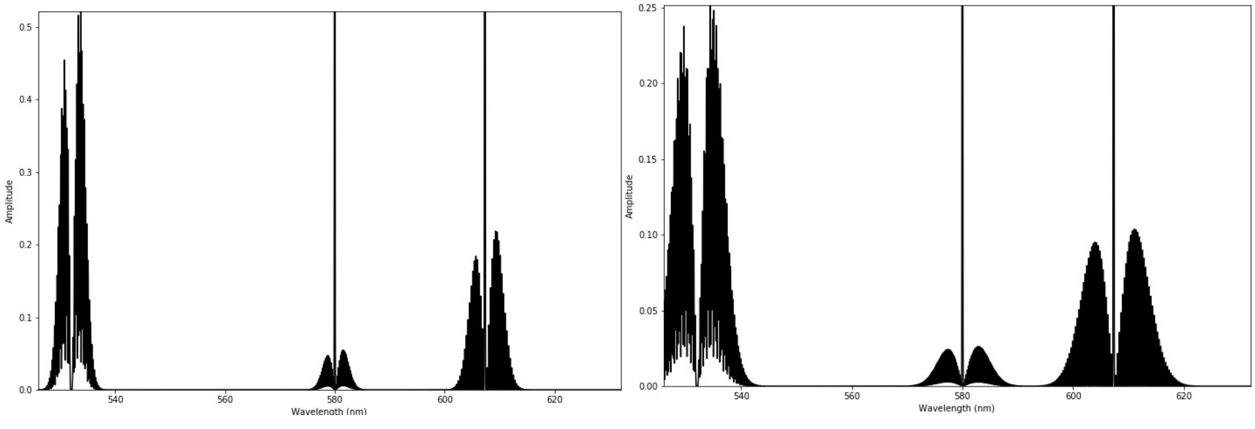
It should also be noted that a large spectral peak will exist at the center of a rovibrational spectrum, where the rotational state does not change. This peak is known as the Q branch, and is typically much stronger than the other branches of the vibrational spectrum.

Using this theory, I have created a python3 Raman spectroscopy simulator capable of generating both the ideal Raman spectrum (as in the actual composition of the light scattered) and the Raman spectrum seen by a detector (which is useful in experimental work, as Raman spectra can be compared to simulated models accurately), of a mixture of arbitrary gasses at arbitrary temperatures. Below are shown a list of examples to visually demonstrate the effects of this theory when applied to the air we breathe. Note that all of these assume the incoming laser has a frequency of 532 nanometers, as would be the case in a frequency-doubled Nd-YAG laser. For purposes of clarity, the intensity axis of the graph will be terminated before the peak of the Q-branch is reached.

Effect of temperature on Raman Spectra

First, below are shown two images designed to show the difference between air at a low temperature (200 K) and air at a high temperature (800 K), which are displayed on the left, and on the right below, respectively. In both spectra, there are numerous similarities that can be used to determine that these spectra were taken from the same gas mixture – The peaks seen both before and after a wavelength of 532 nanometers in both images are the peaks from the purely rotational spectrum. The resolution of this image is high enough, and the distance between the individual rotational lines low enough, that it is possible to individually see the peaks, which leads to the visual artifact of black infill from the sheer number of them. The peaks before and after 580 nanometers are the rovibrational lines for Oxygen, translated to a lower wavelength in proportion to the energy difference between the vibrational energy states of diatomic oxygen gas. The peaks before and after 608 nanometers are formed in a similar way for diatomic nitrogen gas. The extremely high and narrow peaks in the center of the rovibrational spectra are the Q-branches, purely vibrational bands which would dwarf the rest of their respective rovibrational spectra in intensity but were truncated in the plots for ease of view.

However, there are also some major differences. For instance, in the image at 800K, there are about twice as many spectral peaks on either side of the central wavelength. This is because of the changing of the Boltzmann factor with temperature – as temperature increases, higher rotational energy states become significantly more prominent, allowing more molecules to exist in them, which leads to more peaks for the rotational transitions. Although this reasoning also applies to the vibrational energy states, their linear progression makes a transition from the second state to the third absorb the same amount of energy as a transition from the first state to the second, making the two different transitions spectrally indistinguishable. The result of all of this is the spectral signatures for the different gases in the mixture being more pronounced in both the rotational and rovibrational spectra.



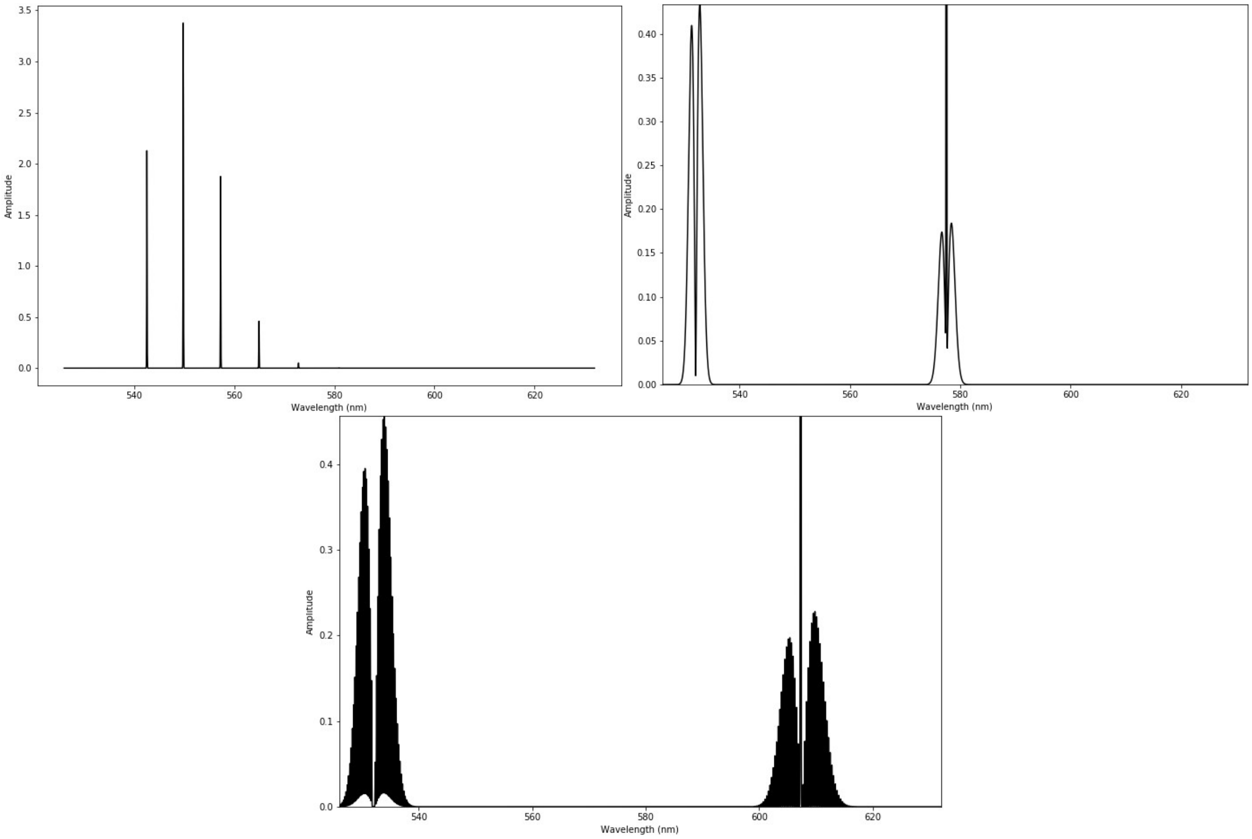
a) Air, 200 K b) Air, 800 K

Effect of composition on Raman spectra

Next, let us compare the Raman spectra of three very different gases – carbon dioxide, diatomic hydrogen, and diatomic nitrogen, all at a temperature of 300 K. As might be noticed below, these three gases have extremely different Raman signatures, although this is most pronounced in the case of hydrogen. The two complimentary oddities of hydrogen stem from the same cause – as quantum effects grow as the mass of the particles in question shrink, it would make sense that diatomic hydrogen, by far the lightest molecule, would have greatly pronounced quantum effects. This comes in the form of having particularly large energy gaps between energy levels, compared to other molecules, for both rotational and vibrational motion. Due to this, only five rotational transitions are visible as thin, nearly vertical peaks on the spectrum, and the rovibrational peaks are not visible at all due to it being hundreds of nanometers longer wavelength than the graph permits, although it should be noted that the rotational peaks are extremely spread-out compared to the diatomic oxygen and diatomic nitrogen in the air shown previously. This makes diatomic hydrogen have an extremely distinctive spectrum.

Regarding carbon dioxide, its spectrum has the opposite rotational effect – as carbon dioxide is much heavier, and much larger than molecules such as diatomic nitrogen, its moment of inertia is much higher, and thus quantum effects are much less prominent. Specifically, the Raman shifts are much lower at constant temperature, and there are many more peaks, so much so that the individual peaks are no longer resolved by the resolution of the graph below, instead forming what looks like only two spectral peaks right before and right after 532 nanometers. The vibrational aspect for spectroscopy for carbon dioxide is even weirder, as the formulae mentioned in the theory previously can only be applied to diatomic molecules. Carbon dioxide, as a linear triatomic molecule, has four different ways that it can vibrate, instead of only one – symmetric stretching, asymmetric stretching, and two modes of bending that are essentially identical yet happen on different axes. Raman spectroscopy actually can only observe vibrational modes where the polarizability (how easily the electron field of the molecule is polarized when exposed to electromagnetic fields) of the molecules changes over time with the vibration process, which is only the case for the mode of symmetric stretching, which is at 1480 wavenumbers. Due to this discrepancy, a manual override had to be placed into the program, which was repeated for non-diatomic gases. As can be seen, this vibrational mode puts carbon dioxide's rovibrational peaks at around 578 nanometers of wavelength.

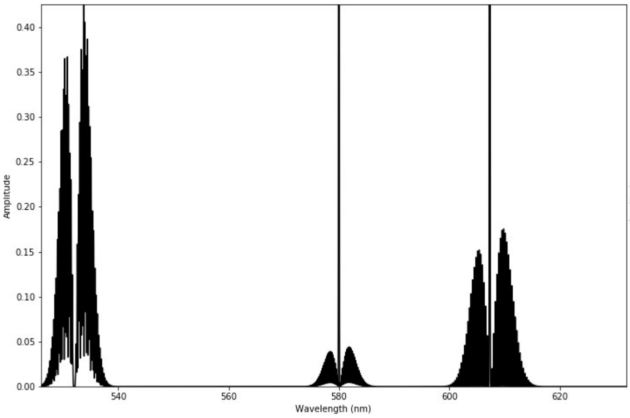
Diatomic nitrogen, as can be seen, is simply the components of the spectrum of air isolated from the rovibrational peaks at 608 nanometers and a large portion of the purely rotational peaks at 532 nanometers for air. This illustrates the principle of superposition in spectroscopy – which states that the spectrum of a mixture of different gases can be found by simply adding the spectrums of the individual gases in their appropriate proportions, such as the diatomic nitrogen in air.

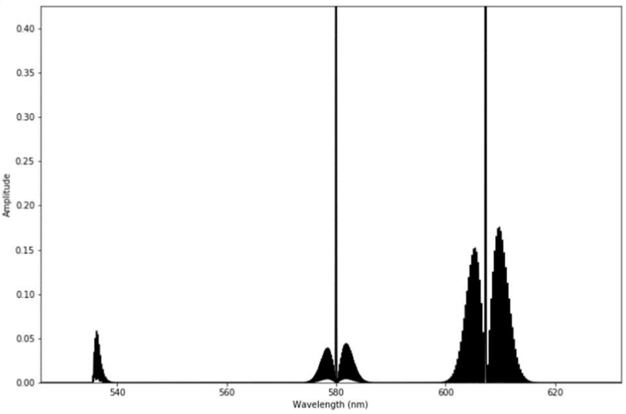


a) H_2, 300 K b) CO_2, 300 K c) N_2, 300K

Long-pass filters

However, the spectrum of scattering being released from the sample is not the same as the spectrum reaching the Raman camera. First of all, there is another process known as Rayleigh scattering, which provides over 99.99% of the light emitted by the sample, while Raman scattering produces 0.01% or less. To prevent excess light from this process from being measured, which would oversaturate the detector, and obscure the rest of the Raman spectrum, a long-pass filter can be used. A filter, in this context, is an optical device used to filter out unwanted frequencies of light before the light reaches the camera. In this case, a kind of filter called a long-pass filter is used, which filters out all light with wavelengths below a certain value. By making this value slightly greater than the wavelength of the light being emitted by the laser, the Rayleigh scattering can be blocked from reaching the camera. However, this method also renders the peaks of the purely rotational spectrum of lower wavelength than the laser invisible, since they are also blocked by the filter. Although all the information stored in the rotational spectrum can also be gotten exclusively from one side of it, making this loss theoretically irrelevant, most realistic filters f this nature dramatically reduce the intensity of the peaks of the purely rotational spectrum at a higher wavelength than the laser, thus making the rovibrational peaks the most informative. Below are two spectra of air at 300 K, one without a long-pass filter (but with the Rayleigh peak redacted, as it would drown the entire spectrum), and another with a long-pass filter between the experiment and the detector. It should be noted that the long-pass filter used in the lab, and thus simulated in the program, is modelled as a filter blocking all light at below 535.5 nanometers of wavelength, and allowing all light to pass at above 536.5 nanometers of wavelength.





a) Air, 300 K b) Air, 300 K, with a long-pass filter

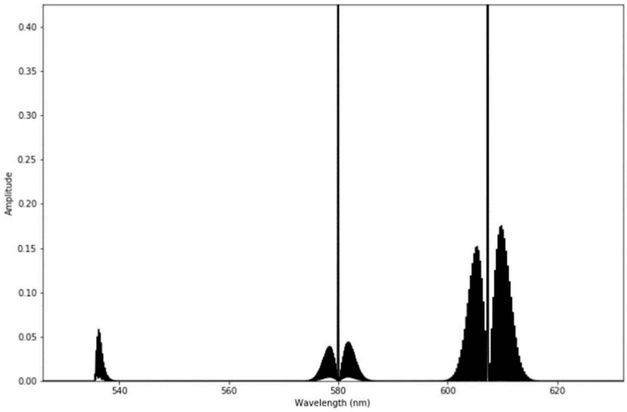
Diffraction gratings and optical equipment

After the light has gone through the long-pass filter, the different frequencies have to be separated to register as different signals on the camera. To do this an optical component known as a diffraction grating is used – a component which utilizes the properties of waves to divert light of different wavelengths at an angle based on the wavelength of the light. This is done by utilizing the fact that light does not behave in intuitive ways once the scale of the environment is similar to the wavelength of the photon. This is typically done in one of two ways, both of which result in the final angle of the light relative to the diffraction grating being functions of the wavelength. The first, and most common way to do this is to use what is known as a reflective diffraction grating, which works by having a repeating pattern of reflective and absorbent surfaces on or near the scale of the wavelengths of light being used, causing the light to be diffracted based on the ratio of the photon wavelength to the repeating length of the pattern on the surface. The second kind, which is the one being used for the Raman spectroscopy experiment, and simulated by the python3 program, uses what is known as a transmissive grating, which works by having a repeating pattern of transparent and opaque surfaces on or near the scale of the wavelengths of light being used, causing the light to be diffracted in a very similar manner, but with the diffracted light being transmitted through the grating instead of being reflected by it. It should be noted that the patterns of color seen on disk storage drives are caused by reflective gratings caused by the immensely dense storage of information of the surface.

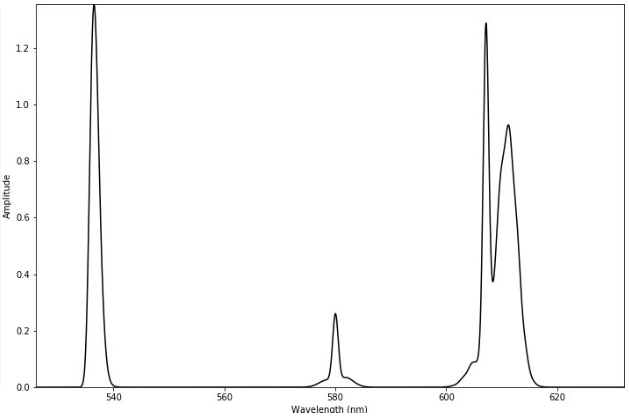
Focusing on transmissive gratings, a mathematical representation of them is required to simulate them in the program. To this end, we will define the variables a, m, λ, θ_{in}, and θ_{out} as the repetition length between the repeating sections of transparency and opacity on the material, the order of the scattering (which is almost always 0, +1, or -1), the wavelength of the photon being analyzed, the angle off of the diffraction grating that the light is arriving at, and the angle off of the diffraction grating that the light is leaving at. The gradient is composed of stripes, so the angles are only measure in the plane perpendicular to the axes of the stripes of the diffraction gradient. Using these variables, the equation $a[\sin(\theta_{out}) - \sin(\theta_{in})] = m\lambda$ can be derived to describe the interaction of light with the gradient. This allows for the image, which previously would have been detected as having only one dimension, corresponding to the position of the scattering on the axis of the laser (which is parallel to the axes of the stripes of the diffraction gradient), to have a second dimension corresponding to the frequency of the scattering, and visible as the axis perpendicular to the axes of the stripes of the diffraction gradient. The program does not simulate the first axis, as it simulated scattering from a point, but does simulate the second axis when determining the necessary resolution of the graph to match the resolution of the Raman camera in the laboratory.

The Raman camera itself uses a complicated apparatus of lenses to transport the light from the scattering through the diffraction grating, and into the camera. To simulate this, optical ray-tracing was used to determine the directions of the light coming though the optical apparatus, and therefore, in combination with the analysis of the diffraction grating, determine the frequency uncertainty based on the width of the grating, the lenses used, and the physical resolution of the camera. To simplify this analysis, all lenses were treated as thin lenses, the small-angle approximation was used, and the transmissive grating was dealt with separately from the rest of the optical apparatus. Below are two spectra of air at 300 K, both with a long-pass filter, but one showing the spectrum as it actually is, and the other showing the spectrum visible to the detector.

As can be seen, the wavelength resolution of the camera (which is simulated as 512px by 512px, and 8mm x 8mm) of 0.52 nanometers drastically limits the accuracy of the spectrum, proving especially problematic for the measurement of the individual peaks in the purely rotational spectrum, as well as the rotational fine structure of the rovibrational peaks. The width of the peaks can still be measured to determine the temperature, though, and the height of the peaks can still be measured to determine the composition, so not much information is actually lost.



a) Air, 300 K, with a long-pass filter



b) Air, 300 K, with a long-pass filter, as observed by the camera

Conclusion

Over the course of this paper, we have covered the quantum theory behind rotational and vibrational spectroscopy, the application of that theory in the changes that result when the temperature and composition of the gas being analyzed are varied, and how that allowed us to extract data from both the rotational and rovibrational spectra. Then, we proceeded to examine the theory behind optical components such as long-pass filters and diffraction gratings, why they were needed, and how they affected the observations of the spectrum. For each of these sections, graphs were provided by my python3 program to illustrate the effects discussed, visually showing the necessary information.