Analyzing Atmospheric Carbonaceous Material Influenced by Wildfires Through Raman Spectroscopy

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Abstract

In 2020, wildfires burned more acreage in the United States than in the past twenty-one years.[1] Boreal wildfires are the cause of ten percent of all annual atmospheric soot in the Northern Hemisphere, which is alarming because soot is detrimental to both human health and environmental health. Some of the negative effects of soot come from the polynuclear aromatic hydrocarbon (PAH) content, which plays a role in the formation of soot. In order to study the structural information of PAH in atmospheric soot from wildfires, a free space Raman spectrometer was built and then used to analyze PAH samples. Raman spectra from anthracene (a PAH), graphite, and o-xylene were collected, showing the spectrometer is in working condition. On collection surfaces, as the height above the fire increased, the areas of dark soot decreased, leading to the belief that the area of observable PAH increases with increasing height. If so, PAH travel farther than soot and spread to greater distances. Suspending the PAH particles in a liquid solution was the most promising method of PAH Raman signal collection and will be improved upon in the future.

Theory of Raman Spectroscopy

Raman spectroscopy studies the vibrational modes of molecules by looking at a unique fingerprint from inelastically scattered light. Individual molecules require various amounts of energy to stretch in certain magnitudes and directions. They absorb this energy through electromagnetic radiation, also known as photons. The energy (E) of a photon is proportional to its wavelength (λ), as seen in Equation 1 where h and c are Planck's constant and the speed of light respectively:

$$E = \frac{hc}{\lambda}$$

Equation 1

When a molecule absorbs the energy from a photon, it excites to a higher energy level. To relax back to a lower energy state, it emits a photon with a specific amount of energy. If the molecule relaxes to the same energy level as it started with, the emitted photon will have the same wavelength as the absorbed photon; this is elastic or Rayleigh scattering of light. Inelastic or Raman scattering happens when the molecule relaxes to a different energy level than it started at. Therefore, the emitted photon is a different wavelength and energy was either gained from or lost to a molecular vibration. There are two types of inelastic scattering: Stokes and anti-Stokes. Stokes scattering is when the molecule relaxes to a higher energy level than it started, so the emitted photon has a lower energy and a longer wavelength – it is red shifted. Anti-Stokes scattering is when the molecule starts in an excited state, and then relaxes to a lower energy level than it started. The change in energy is larger when relaxing, so the emitted photon has a higher energy and a shorter wavelength than the absorbed photon – it is blue shifted. Because the molecule must be in an excited state before absorbing a photon, anti-stokes scattering is weaker and more difficult to detect.

Raman spectrometers excite a sample with a laser and collect the inelastic scattering of light to produce a spectrum. The peaks in the spectrum represent the energy changes between vibrational states of the sample molecule. However, it is estimated that only one in every ten million photons are Raman scattered - the Raman signal is very weak and will get drowned out by the elastic scatter.[2] Since the elastic scatter is the same wavelength as the laser, it can be blocked by a notch filter made for the wavelength of the excitation laser. The spectrometer in this

experiment was focused on collecting Stokes scattering, so any light at or smaller than the excitation laser's wavelength was filtered out. The remaining light is collected for analysis.

Introduction

In 2020, 58,258 wildfires burned 10,274,679 acres across the United States. This was the most acreage burned on record in 21 years, and it's only predicted to get worse.[1] Wildfires have many negative effects, one of which is soot emissions. Ten percent of all annual atmospheric soot emissions in the Northern Hemisphere are from boreal wildfires.[3] This is a problem because soot absorbs solar radiation, contributing to global warming. Soot's negative effects on humans can be seen through higher rates of respiratory diseases and cancer in urban areas that have high amounts of air pollution from incomplete combustion processes resulting from industry, fires, cars, etc.[4] In a perfect world, combustion forms only carbon dioxide and water. In practice, combustion is not perfect, resulting in the formation of soot and polynuclear aromatic hydrocarbons (PAH), many of which are known carcinogens.[4]

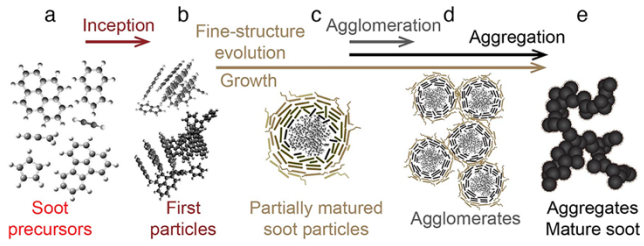

Figure 1. Diagram of the major steps in soot formation[4]

The compositions of hydrocarbon fuels and mature soot aggregates are well known, but there are discrepancies in the literature about how the 2D growth becomes 3D growth. One of the main theories of how soot forms from PAH is explained below and shown in Figure 1.[5] The soot formation process starts with PAH, which are based on six membered planar hydrocarbon rings, such as benzene, coronene, or anthracene. At some point during this growth, the PAH begin to stack into first particles. The first particles will then stack to make spheres of particles. The spheres will agglomerate into groups, which aggregate into mature soot that grows big enough to see without magnification. This work focuses on the inception stage of soot.

Since 1970, there has been precedence in the literature that Raman spectroscopy can be used to study the size of carbonaceous material. Raman spectroscopy studies the vibrational modes of molecules, and for graphitic materials (benzene rings repeating in a plane) there are two vibrational modes: the ring breathing mode (D mode) and a ring stretching mode (G mode), shown in Figure 2. Raman spectra of carbonaceous material have been used to look at samples collected from highly controlled flames in a laboratory setting, therefore analyzing a more chaotic setting was needed.

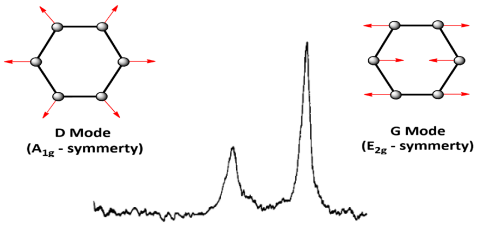

Figure 2 – Example spectrum from graphite – like materials. Vibrational modes that cause each peaks are shown next to their respective peak[4]

Raman spectroscopy was used to explore structural information of PAH from the air above wildfires. It was predicted that the area of observable Raman signatures would increase with increasing height. Small PAH should travel farther than heavy soot, in the process spreading carcinogens greater distances. The PAH size was predicted to be approximately the same with increasing height above the fire because once the PAH are out of the fire it would have less energy, so stacking would occur instead of chemical growth. These results are important because understanding how wildfires impact the atmosphere may lead to techniques to decrease their effect.

Methods

Raman Spectrometer Design

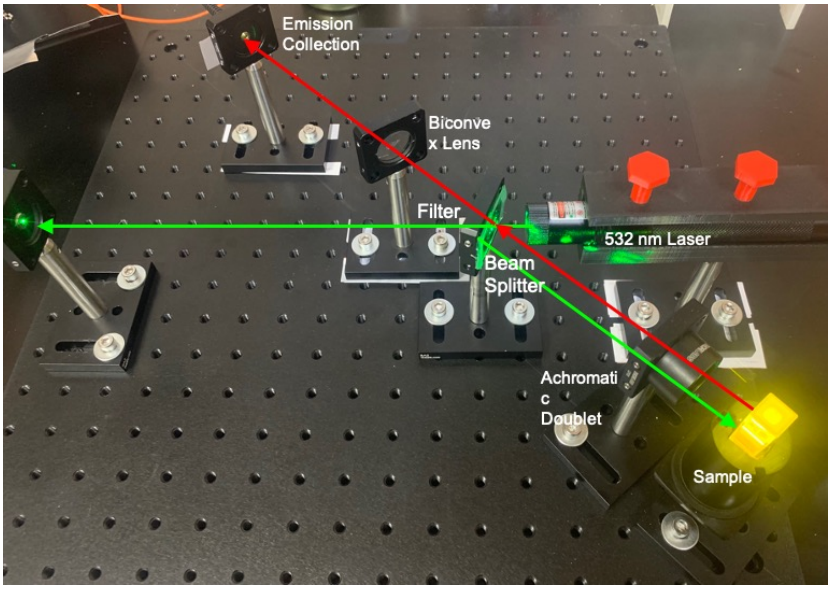

Figure 3 – Picture of the Raman spectrometer design. Light direction is shown with arrows. Green arrows represent the original laser light and red arrows represent the fluorescence. Components are labelled.

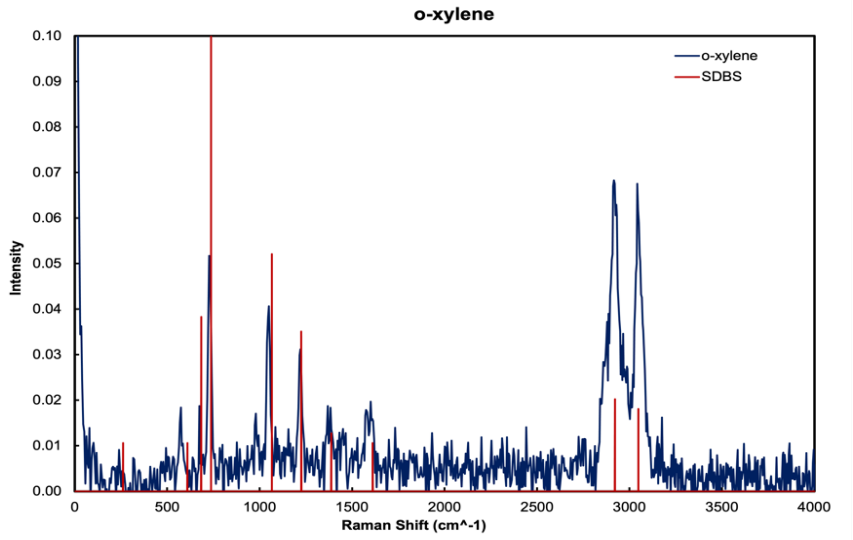

Figure 4 – Experimental spectrum from o-xylene (blue) compared to values from the Spectral Database for Organic Compounds by AIST (red).

Many arrangements of the optics were tested, but the arrangement shown in Figure 3 allowed for the strongest Raman signal. Light from a <1000 mW 532 nm laser was directed through a beam splitter (microscope slide); 30% of the light shines through the beam splitter and 70% of the light is reflected towards the achromatic doublet, where it is focused onto the sample. Emissions from the sample then pass through the achromatic doublet again, in this case acting as a collimator by redirecting the unfocused scattered light from the sample into parallel light rays. This way, less light will be lost while travelling from the excited sample back through beam splitter, which has a 550 nm longpass filter on the back to block the elastically scattered and laser light. The parallel rays then pass through the biconvex lens, which focuses the light into a single point. The emission is collected on to a fiber optic cable at this focal point in order to deliver it to the spectrometer. Inside the spectrometer, the light will reflect off a diffraction grating that separates the light into its individual wavelengths. A charge coupled device (CCD) then translates the photons into electrical signals that can be read and plotted by a computer. Once built, the spectrometer was aligned by maximizing the fluorescence from a solution of ethanol and red Sharpie ink in a cuvette. To ensure correct alignment, a Raman spectrum of o-xylene was collected and compared to the literature (see Figure 4).

Sample Collection

The original setup for collecting soot samples is shown in Figure 5, which in inside a fume hood. A fire is lit on the watch glass and the air duct directs the smoke onto the filter paper, which is placed 3 cm above the fire to promote air flow. The fire was made from 1 g of dead Aspen leaves and 1.5 g of dead pine needles that were collected from outside the lab. The air duct is flexible so it can be adjusted to 10, 15, or 20 cm for each trial. Filter paper, construction paper, sticky notes, copper wire mesh, titanium plates, and aluminum wire were tested as collection surfaces.

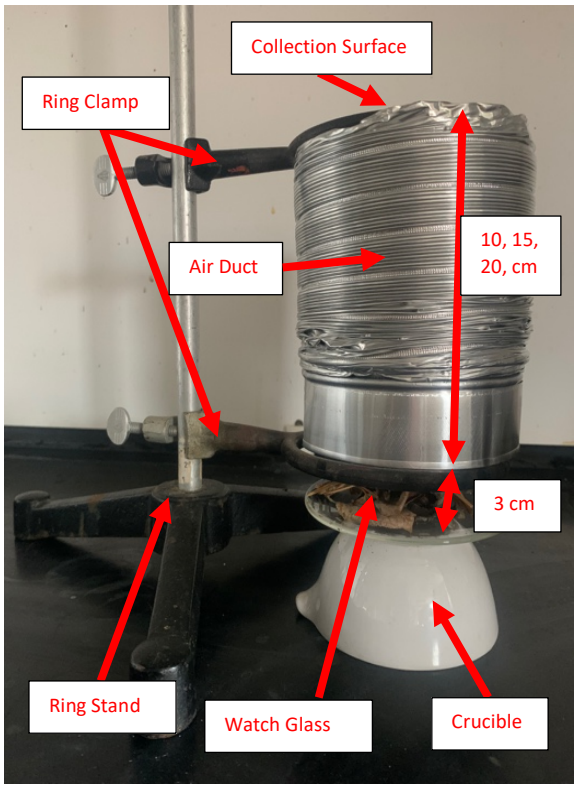

Figure 5 – Picture of the setup for collecting soot samples.

To test a clear surface, powdered soot stirred into soapy water was poured onto a microscope slide and left to evaporate for 24 hours. A background slide of plain soapy water was left to evaporate as well.

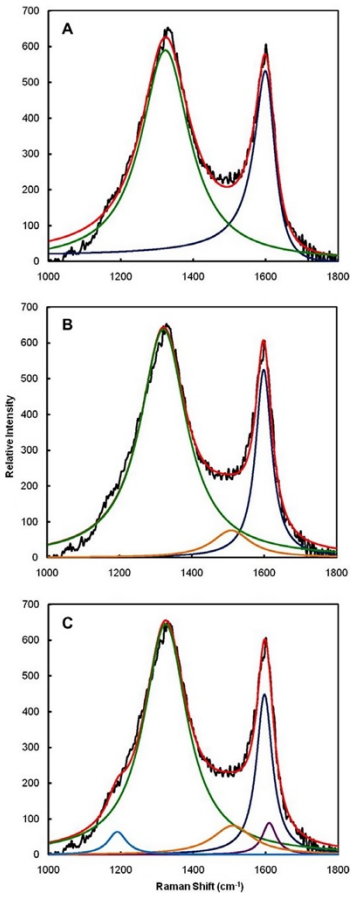

Figure 6 – One PAH example spectrum with three different fitting parameters. An in-depth explanation is in the Tables and Figures section.[7]

PAH suspended in liquid was also tested. To extract the PAH, ash was refluxed in a toluene/ methanol (1:6) solution and a cyclohexane/acetone (1:1) solution.[6] For each solution, half a gram of burnt Aspen leaves were put into a round bottom flask and refluxed with 40 mL of solution for four hours. The solution was then double filtered through Whatman 42 filter paper, which filters down to 0.7 microns. This is small enough to catch any soot particles, but the PAH will be able to pass through with the solution. The final solution containing the PAH was analyzed in the spectrometer.

Techniques for Signal Collection from Sample

To collect a clean signal, the background spectrum must be subtracted from the sample spectrum. To obtain the sample spectrum, 30-50 second integration times were used depending on the signal strength and the florescence of each sample. Background spectra were taken for the same amount of time with the same materials as the sample holder and subtracted from the sample spectra.

Analysis

The background subtracted spectra will be fit to the two G and D mode peaks. Software written using a simplex algorithm in a Delphi (PASCAL) computer program has been created with multiple ways to fit these bands. While a two-band fit is anticipated, the fitting parameters will be explored to find the best fit once Raman spectra of

PAH are acquired. An example spectrum from PAH and the different ways to fit a spectrum are shown in Figure 6[7]. Once fitted, the ratio of the intensities of the D band and G band can be calculated (see Equation 2). This ratio is proportional to the conjugation length (L_a) of the PAH, which is the length of the longest aromatic chain in the molecule. Width and location of peaks will also be analyzed for patterns and insights.

$$\frac{I_D}{I_G} \propto L_a$$

Equation 2

Hazards and Safety

Lasers can cause permanent and immediate blindness. Never look directly at a laser or a reflection of the laser. Remove any reflective jewelry like rings or watches. Skin burning is also possible from the localized heat produced in the laser beam. The laboratory should be properly labelled with laser warnings and people should not enter the lab if the laser is in use. Fire precautions should be taken when collecting the fire samples. Fires should only be lit inside an empty fume hood with the sash closed most of the way.

Results

A Raman spectrum from Graphite yielded a G peak (see Figure 7). A Raman spectrum from anthracene, a small, 3-ring PAH, was collected that matched the database values (see Figure 8). Spectra was collected from solid anthracene multiple times.

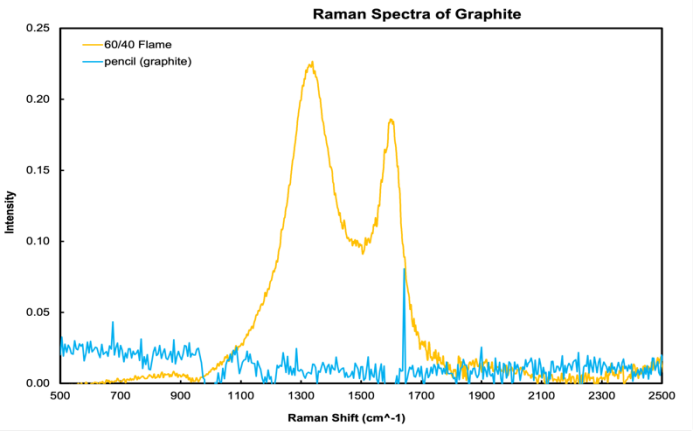

Figure 7 – Experimental graphite spectrum (blue) with a G peak compared to a hydrocarbon flame sample (yellow) with a D and G peak.

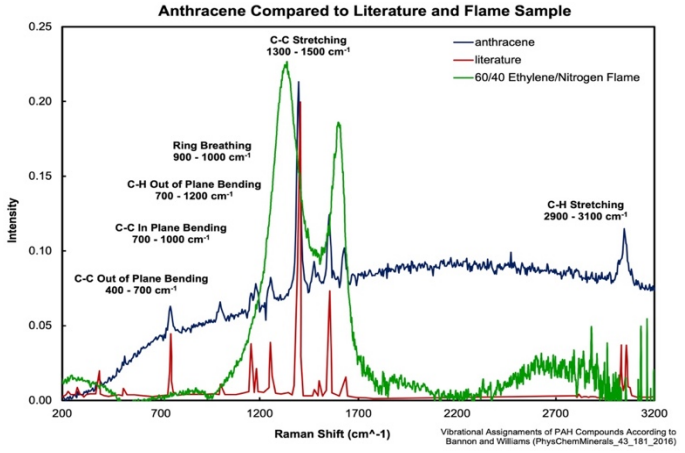

Figure 8 – Experimental anthracene Raman spectrum (blue) compared to literature values (red) and a flame sample (green).

All types of paper fluoresced and drowned out any possible PAH Raman signal. No signal was collected from any metal surface or microscope slide. The acetone in the cyclohexane/acetone (1:1) solution melted the plastic cuvette when the sample was being analyzed and there was a large fluorescence peak. The toluene/methanol (1:6) solution also had a large fluorescence peak, covering any possible PAH signal.

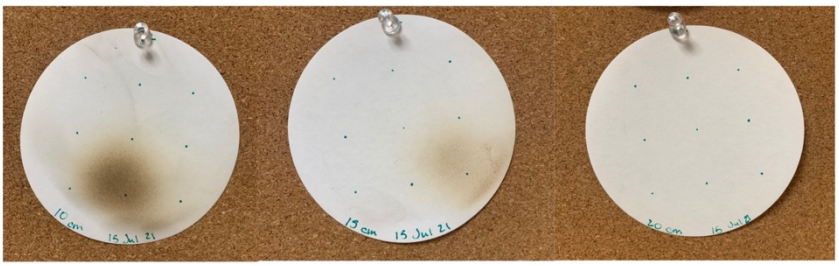

Figure 9 - Original filter paper samples show the area of observable Raman signatures increasing.

The area of soot collection increased as height above the fire decreased, as predicted. This leads us to believe that we will be able to observe larger areas of PAH Raman signatures (see Figure 9).

Discussion

The G peak signal from graphite shows the spectrometer is capable of collecting a signal from PAH. However, a signal from the PAH has not been collected. Both types of paper fluoresced too much to use. The metal surfaces did not work either, although they did not fluoresce. The literature shows a PAH Raman signal from a metal surface can be collected, but it is harder because it is a 2D surface.[7] Free space Raman works best with 3D liquids because a volume is analyzed.[8] When the laser can pass through the entire depth of the cuvette, the sample only has to be close to the focal point of the achromatic doublet, not exact. The focal point will be somewhere within the depth of the liquid. The PAH samples on 2D metal must be placed at the exact focal point and at an exact perpendicular angle to the emission collection in order for the collected Raman signal to be strong enough to observe. Therefore, the difficult to collect Raman scattered light becomes even more difficult on a planar surface. If there were fine tune adjustments on the spectrometer a signal might have been collected, but with the tools available it was not possible to collect a Raman spectrum from a metal surface.

However, an accurate solid anthracene signal was collected, so the Raman spectrometer can be used on some solids. Anthracene is slightly transparent, so some of the laser was passing through, making it easier to collect this spectrum. In the future, pressing the solid soot sample into a pellet will be tested to get a more reliable signal from a solid.

Suspending the PAH in a liquid solution proved to be the most promising method of sample collection. Acetone is a corrosive material, which the plastic cuvette is sensitive to. However, fluorescence was observed before the plastic melted completely. The toluene/methanol (1:6) showed the same fluorescence peak. Methanol is also corrosive like acetone, but the sample was in a quartz cuvette which was not affected by the solution. The fluorescence of both solutions was not in the background spectrum, so the reflux process worked and extracted carbonaceous material into the liquid. However, the fluorescence must be decreased in order to see the PAH spectrum. This problem will be solved with continued research.

As height increased, the area of observable soot decreased; it is expected that this means PAH signatures will increase. If true, PAH travel farther than the fully matured soot in the air. This outcome is concerning because locations that are too far away from wildfires to see smog might still be affected by the carcinogenic PAH content. The method for testing air quality usually looks at the concentration of aerosol particles under 2.5 microns in size, which are things big enough to see like smog.[9] However, the concentration of particles under 10 nanometers should be looked at more closely, as this includes the smaller particles like PAH that still affect health but can’t be seen.

While experimenting, many questions for future research presented themselves. How far above a flame will PAH travel, and is the relationship between PAH height and fire size exponential or linear? Does the structure of PAH change when the fire is flaming compared to smoldering? Do the PAH interact with the atmosphere, leading to more oxygen or nitrogen signatures when farther above a flame?

There were many opportunities for error during this research. The original filter paper used could only filter particles over 0.7 microns in size, which is bigger than any PAH. The samples were not covered with aluminum foil, so sunlight might have altered the structure of the molecule. The laser is also very powerful and might be altering the sample. Another source of error is the lack of fine tune adjustments on the spectrometer. Without fine tuning, some signal is lost. In the future, we hope to upgrade to kinematic mounts, which will allow the alignment process to be more exact. We also hope to fiber couple the laser so it can be switched to various excitation wavelengths without realigning the entire optical setup.

We plan to continue the research during the fall 2021 semester and hope to find more specific PAH results. If a Raman spectrum is able to be collected from PAH samples during the fall, the original question will be answered, and the future experiment's questions listed above will also be tested.

Acknowledgements

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Tables and Figures

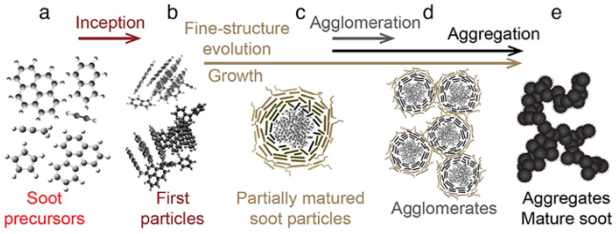
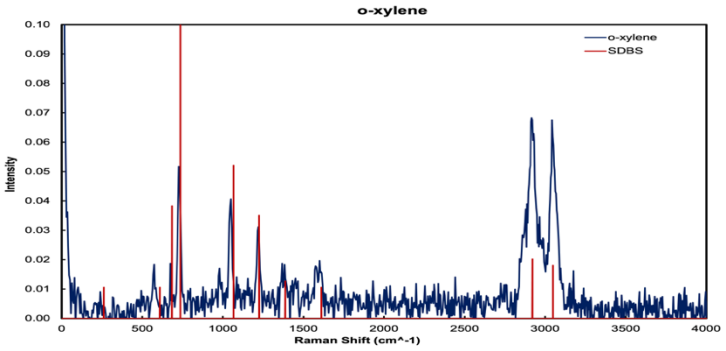


Figure 3. Diagram of the major steps in soot formation[4]



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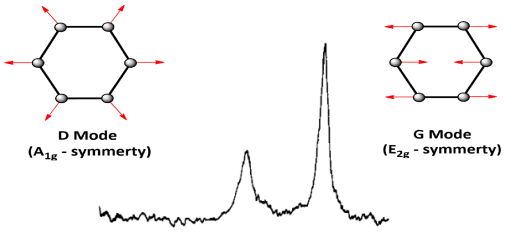

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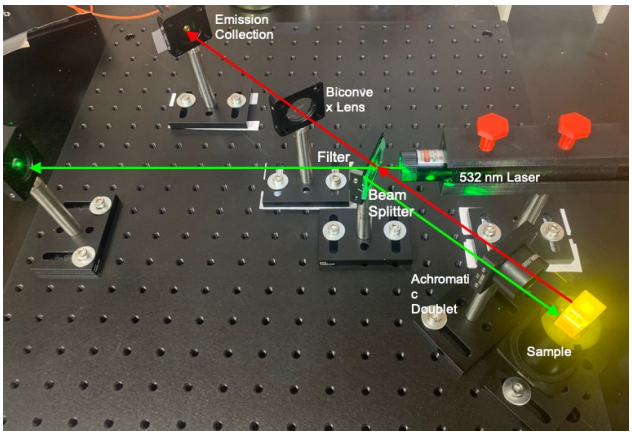

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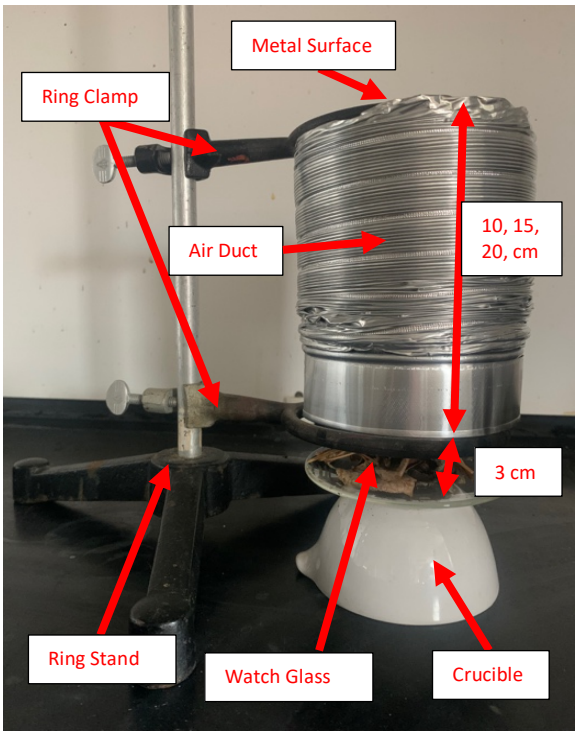

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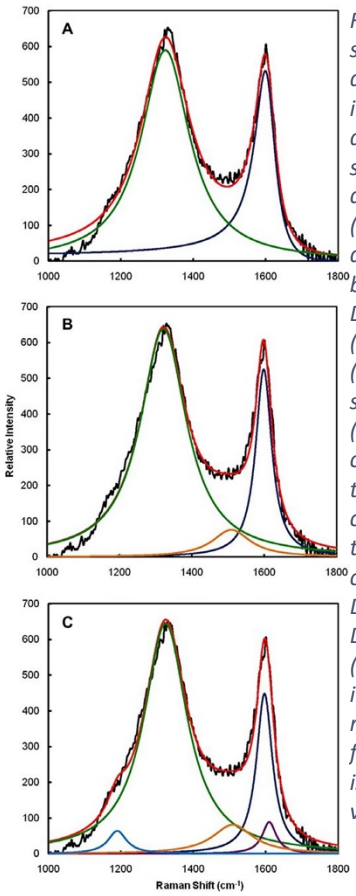
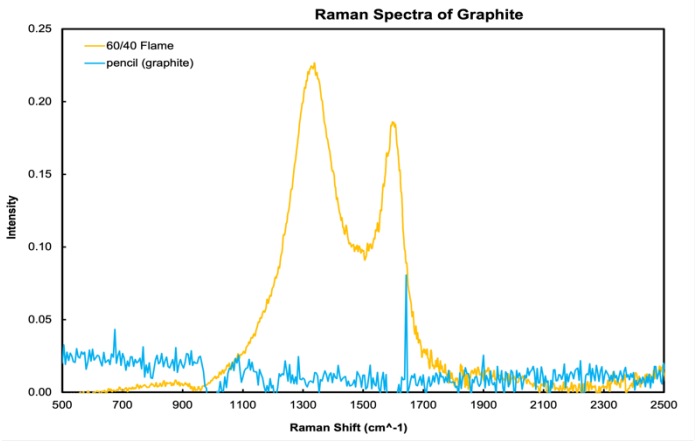


Figure 6 - Example spectra for PAH. Three different fitting schemes investigated to deconvolve Raman spectra: D1 (Lorentzian) and G (BWF) two-band fit (A); D1, G (Lorentzian), and D3 (Gaussian) three-band fit (B), and D1, D2, D4, G (Lorentzian) and D3 (Gaussian) five-band fit (C). In each panel are shown the raw data (black), fit spectrum calculated by summing the individual peak contributions (red), and the individual peak contributions [D1 (green), D2 (purple), D3 (orange), D4 (light blue) and G (dark blue)]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)[9]



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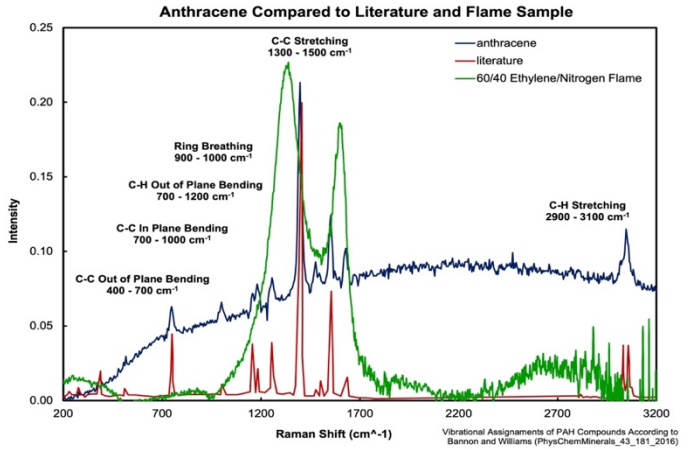

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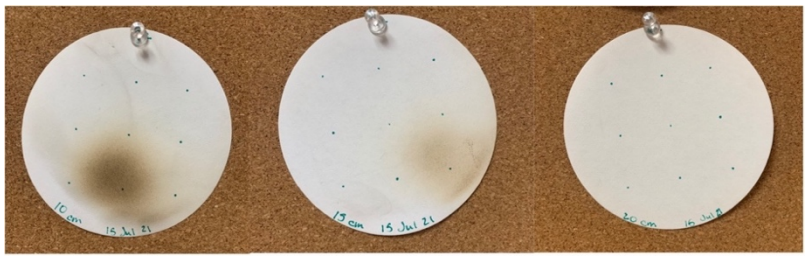

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