

Advanced Measurement Techniques in Fluid Mechanics and Heat Transfer

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Week – 10

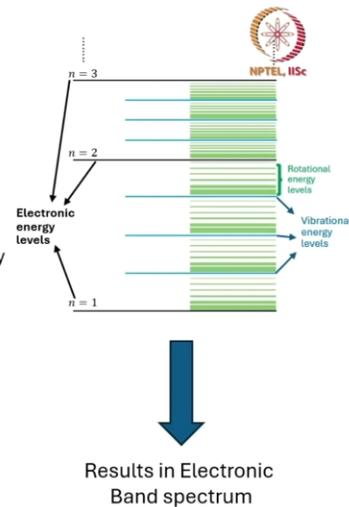
Lecture - 50

Emission Spectroscopy – 2

In the previous lecture, which is in part 1, we discussed luminescence, why it occurs, and what the different examples in real life are where we see luminescence. Later, we discussed electromagnetic radiation, its characteristics, what the electromagnetic spectrum is, and then spectroscopy. In spectroscopy, we looked at two types of spectra: line spectrum and continuous spectrum. A continuous spectrum is where the electromagnetic radiation contains all the wavelengths, while in a line spectrum, the incident light contains only specific wavelengths corresponding to specific electronic transitions that have occurred in the atom that emitted it. We have used Bohr's model to explain the different electronic transitions corresponding to different spectra by taking hydrogen as an example. However, this model is not sufficient to explain the complex interactions and transitions that occur in atoms with a higher number of electrons, as well as in complex molecules.

Molecular spectroscopy

- Molecular spectra are often more complex than atomic spectra due to the additional vibrational and rotational energy levels.
- This complexity leads to a larger number of closely spaced lines, sometimes appearing as bands rather than individual lines in the emission spectrum obtained from the molecules.
- When the excited molecule returns to a lower energy state, it releases the excess energy in the form of electromagnetic radiation (light).
- The emitted light can have different wavelengths depending on the specific transitions between different energy levels of molecules:
 - **Electronic Transitions:** Result in emission in the visible, ultraviolet, or infrared regions.
 - **Vibrational Transitions:** Result in emission in the infrared region.
 - **Rotational Transitions:** Result in emission in the Far-infrared to microwave region (*low energy*).
- Molecular spectra can be very complex due to factors like:
 - Interactions between different types of energy levels.
 - Interactions with other molecules (e.g., collisions), Isotope effects, etc.



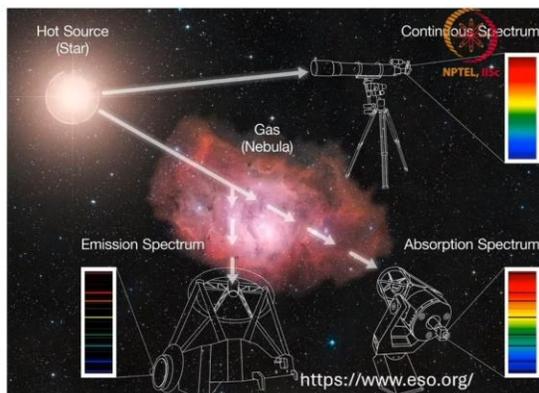
In today's lecture, we'll be briefly going through molecular spectroscopy, and later we will discuss the applications of spectroscopy; further, we will discuss specific concepts of

where this spectroscopy is used in scientific research, and finally, we will discuss chemiluminescence, which is one of the experimental techniques based on emission spectroscopy. Now, we will discuss molecular spectroscopy. Previously, we have discussed the emission spectroscopy of atoms, specifically for the hydrogen atom, and we have mentioned that Bohr's model can be used to estimate the different electronic transitions corresponding to different spectral lengths in the emission spectrum. but this is accurate only for hydrogen atoms and the model becomes too simple to explain atoms with a higher number of electrons; in molecules, the energy states are not only limited to the electronic states and the energy levels, but other energies such as rotational energy and vibrational energy also exist.

This makes molecular spectroscopy complex. So this complexity leads to a large number of closely spaced lines, sometimes appearing even as bands rather than individual lines in the emission spectrum obtained from the molecules. Similar to atoms, when the excited molecule returns to a lower energy state, it releases excess energy in the form of electromagnetic radiation. However, emitted light can have different wavelengths depending on specific transitions, which are not only electronic transitions but also vibrational and rotational transitions. Here in the schematic, it can be seen that the dark lines corresponding to n equal to 1, n equal to 2, and so on are the electronic energy levels, whereas the light blue lines.

Applications of Spectroscopy

- Spectra can be used to detect, identify and quantify the information about the atoms and molecules in various fields from astronomy to biochemistry.
- Astronomy: Spectroscopy can be used to analyze the spectra radiation emitted by distant stars, galaxies, planets, etc.
 - To find chemical composition, physical properties like temperature, density, etc.
- Environmental Science: Remote sensing, pollution, soil composition, vegetation, etc. using satellite imaging.
- Material Science: Characterization and quality control of metals, polymers, semiconductors etc.
- Chemical kinetics: Kinetics and chemical reactions are analyzed by studying the emissions from the molecules and radicals involved.
- Biochemistry: Protein structure, DNA analysis, diagnostic tool, etc.
- Identifying unknown substances and quantifying elements and compounds.



- Specific wavelengths are absorbed by different elements producing dark lines over the line spectrum continuum (**Absorption spectrum**).
- Energy thus absorbed is then re-emitted in all directions producing bright lines. (**Emission spectrum**).

.. Are the different vibrational energy levels present within those electronic energy levels, and are there further, more closely spaced rotational energy levels within these, which are

denoted by green lines? So the transitions in molecules may occur between different electronic energy levels or between different rotational energy levels within an electronic energy level. Or between different vibrational energies within electronic energy levels, or even the combination of rotational energy levels to vibrational energy levels within or between different electronic energy levels, and so on, the electronic transitions result in the emission of visible light, ultraviolet light, and infrared light because the energy gap is high compared to. Vibrational and rotational transitions. The rotational transitions have the longest wavelength corresponding to the lowest energy because they are closely spaced. The molecular spectra can be very complex due to these factors, and other factors that can affect them are collisions and isotope effects.

In the previous slide, we have seen why molecular spectroscopy results in a complex line spectrum where the lines are so closely spaced that they can even appear as bands. This is because of the presence of different rotational and vibrational energy levels in addition to electronic energy levels, which are closely spaced with each other. Here on the right side, emission spectra for different elements and molecules have been provided, and here we can see that from top to bottom, as we increase the complexity of the system, helium is the simplest system with a single atom and two electrons, followed by xenon with a large number of electrons and water vapor with three molecules. We can see that in the case of helium, the spectrum looks like a line spectrum with discrete individual lines at specific wavelengths; however, there are closely spaced lines that appear as bands. Even in helium, when we go to hydrogen, the system is more complex because, even though it has the same number of electrons (that is, two) as helium, here the hydrogen molecule contains two atoms with a pair of energy levels of their own, which results in a large number of electronic transitions.

Occur in hydrogen molecules resulting in lines in the spectrum that are so closely spaced that they appear as bands; similar is the case for other complex systems. As you can see, now coming to the applications of molecular spectroscopy, molecular spectroscopy, because of these emissions and these spectra, provides insights into the structure, properties, and behavior of molecules. As we have already discussed, both rotational and vibrational modes will also contribute to the emissions of the spectrum, so the emissions will also give insights into the vibrational and.

.. Rotational modes, which indirectly give us information about the orientation and shape of the molecule and the arrangement of the atoms in the molecule, are important. Some of the applications for molecular spectroscopy include the identification and analysis of unknown compounds and determining their structure. Quantitative analysis is another application; if we have a solution or a mixture with a specific concentration of a given molecule, then molecular spectroscopy can be used to measure the concentration of a

specific molecule in a sample. Another example is chemical kinetics, where reaction rates and mechanisms can be studied using spectroscopy while a reaction takes place. Now let's discuss the applications of spectroscopy.

Spectra can be used to detect, identify, and quantify information about the atoms and molecules in various fields, from astronomy to biochemistry. In astronomy, spectroscopy can be used to analyze the spectra of radiation emitted by distant stars, galaxies, and planets. This can be used to find the chemical composition and physical properties, such as temperature and density. Of distant astronomical objects. In environmental science, dynamic sensing, pollution, soil composition, and vegetation, etc.

It can be obtained using satellite imaging, and this also works based on spectroscopy. In materials science, characterization and quality control of metals, polymers, etc. It can be done using spectroscopy. Chemical kinetics is one of the important areas where spectroscopy gives us insights into kinetics, chemical reactions, and the presence of intermediate radicals—unstable species that emit radiation during the reaction. In biochemistry, protein structure, DNA analysis, and diagnostic tools use spectroscopy.

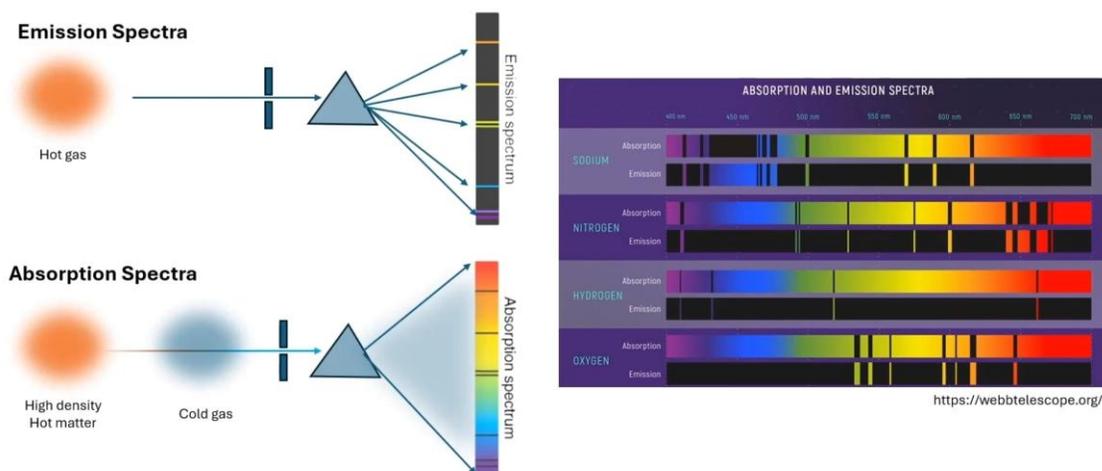
In all these applications, identifying unknown substances and quantifying elements and compounds are key applications for spectroscopy. As we can see in the picture provided on the right side, the schematic shows that the light that directly comes from a hot source, such as a star, when it reaches Earth and the spectrum of that light is captured, probably shows a continuous spectrum; however, when the light from the hot star passes through a gas nebula, which is a dense cloud of gas, this gas absorbs energy from the light as it passes through. After this energy is absorbed by the gas, If the light transmits through this gas cloud and that transmitted beam is captured, and the spectrum of that is obtained, then it shows a continuous spectrum with black lines on it. These black lines correspond to the specific wavelengths corresponding to the energies that the gas has absorbed. On the other hand, once the gas molecules absorb this energy from the incident light, the molecules or atoms get excited, and when they come back to the ground state, they emit that energy as radiation as well, and when this emission is captured, the spectrum is obtained.

This looks like something that we have already discussed, in which bright lines are present on a dark background. When bright lines are present on a dark background, it is called an emission spectrum because it is emitted by the gas molecules after the molecules de-excite to the ground state. Whereas the spectrum that is obtained directly from the transmitted light from the star, which has passed through this gas nebula, is called the absorption spectrum because dark bands corresponding to the energy absorption by the gas nebula are present in this spectrum. Now let's discuss the two types

of spectra that we have seen: the absorption spectrum and the emission spectrum. In the emission spectrum, as we have discussed before, the molecules in a hot gas emit radiation when they return to a lower energy state, and this radiation, when passed through a slit and converted to a beam, then passes through a prism, causing the different wavelengths present to be deflected.

As we have already explained, the longer wavelengths deflect at shallower angles, whereas the shorter wavelengths deflect at steeper angles. This produces a line spectrum where different wavelengths present in the incident light emitted by the hot gas form individual discrete lines on the spectrum. Since only these specific wavelengths are present in the incident light, the rest of the spectrum appears dark. Now, coming to the absorption spectrum: when high-density hot matter, such as a star, emits radiation, that radiation contains all the spectrum, all the wavelengths. However, when that emitted light is allowed to pass through a gas cloud, the molecules in the gas cloud absorb some energy from that light.

Absorption vs Emission spectra



Allow the transmitted light, after the energy has been absorbed, to pass through the prism; we obtain an absorption spectrum. In the absorption spectrum, we see a continuous spectrum of different wavelengths that are originally present in the emitted light from the star. However, dark lines are seen in the spectrum corresponding to the individual wavelengths that pertain to the energy transitions that occur when the energy from the incident light is absorbed by the molecules in the gas cloud. The different emission and absorption spectra for different elements have been shown on the right side.

Where we can see in the absorption spectra, dark lines or bands are present on a continuous spectrum, whereas in emission spectra, bright lines or bands are present on a dark background.

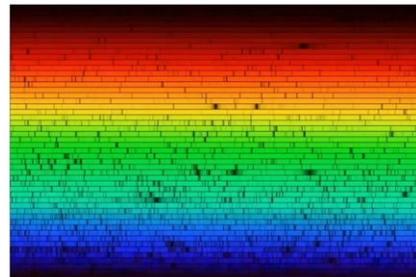
We can clearly see here that, for all the cases, the absorption and emission spectra complement each other; that means the summation of the absorption and emission spectra should give us a continuous spectrum. Thus, to summarize, the initial energy radiation that is directly coming from the star, which is incident on the gas cloud, initially has a continuous spectrum. However, when this radiation passes through the gas cloud, the energy is absorbed by the molecules inside the gas cloud, leading to the excitation of those molecules. Subsequently, the gas cloud molecules return to the ground state and emit radiation having discrete light lines on the transmitted spectrum. This is nothing but the emission spectrum corresponding to the molecules in the gas clouds.

On the other hand, the spectrum of the initial radiation after the energy has been absorbed by the gas cloud, which is the spectrum of the transmitted light, is an absorption spectrum that has dark discontinuities on a continuous spectrum. Thus, the emission and absorption spectra complement each other because the same energy levels and transitions are involved in both cases.

Absorption vs Emission spectra



- The initial energy radiation from the star incident on a gas cloud is **continuous spectra**.
- This energy is absorbed by the molecules leading to their excitation to higher energy states and subsequently, the gas cloud molecules return to the ground state, and emit radiation having discrete bright lines on a dark spectrum (**emission spectrum**).
- On the other hand, the spectrum of the incident radiation after the energy absorption by the gas cloud i.e., transmitted light radiation is called **absorption spectrum** (dark discontinuities on a continuous spectrum).
- Thus, the emission and absorption spectrum complement each other, because the same energy levels and transitions involved in both are same.
- Hence, Emission and absorption spectrum together form a continuous spectrum, and this is taken advantage of in fields like astronomy by indirectly estimating the composition of planets using absorption bands compared to the continuous spectrum of the light from the star.
- Even the spectrum of solar radiation also shows dark absorption bands, which provide information about the chemical composition and temperature the sun,



McMath-Pierce solar telescope,
National Solar Observatory, Arizona.

Hence, the emission and absorption spectra together form a continuous spectrum, and this is taken advantage of in fields like astronomy by indirectly estimating the composition of planets using absorption bands compared to the continuous spectrum of the light from the

respective star. It is interesting to note that even the solar spectrum we receive from the sun shows dark absorption bands that provide information about the chemical composition and temperature of the sun itself. Here we can see the image on the right side, where this is a solar spectrum.

Even though the light coming from the star originally has a continuous spectrum, as the light passes through the hot gases and exits the sun's atmosphere, those gases in the sun's atmosphere absorb different energies from that radiation, thus forming these discrete dark patches or discrete dark lines in the solar spectrum. Thus, the spectrum that we receive from the sun is effectively an absorption spectrum if the corresponding photon originated at the core of the sun and has to travel through different layers of the sun before reaching Earth. Thus, the dark lines or patches present in the solar spectrum can be used to estimate the composition of different layers of the sun and other properties such as temperature, density, etc. Now, let's discuss Beer-Lambert Law.

The absorption of energy in incident radiation as it passes through a medium can be understood using Beer-Lambert's law. It is a fundamental principle in spectroscopy that relates the attenuation of light to the properties of the material through which the light is traveling.

Beer Lambert's Law



- The absorption of the energy in an incident radiation as it passes through a medium can be understood using Beer Lambert's Law.
- It is a fundamental principle in spectroscopy that relates the attenuation of light to the properties of the material through which the light is traveling.
- Mathematically, Beer Lambert's law is expressed as: The light intensity of a monochromatic light radiation exponentially decreases with the travel distance through the medium and the concentration of the absorbing substance, as it passes through the transparent medium.

$$A = \log \frac{I_0}{I} = \epsilon c l$$

where,

A = Absorbance

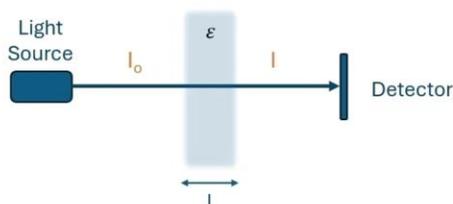
I_0 = Intensity of the incident light

I = Intensity of the transmitted light

ϵ = Molar absorption coefficient

c = Concentration of the sample

l = travel distance through the medium



- Transmittance, $T = \frac{I}{I_0}$
- The transmittance of a radiation through a medium can be used to estimate the concentration of a compound with known absorption coefficient in a transparent mixture.

Mathematically, Beer-Lambert's law is expressed as the light intensity of monochromatic light radiation exponentially decreases with the travel distance through the medium and the concentration of the absorbing substance as it passes through the transparent medium.

So the relation is shown here in mathematical terms as A , which is the absorbance that is the logarithm of the ratio of the initial radiation intensity and the radiation intensity after passing through the medium; thus, absorbance is equal to ϵcl , where ϵ is the molar absorption coefficient, c is the concentration of the sample, and l is the travel distance through the medium, which is the width of this medium. Here, the transmittance is I/I_0 , which is the ratio of the transmitted radiation intensity to the incident radiation intensity.

The transmittance of radiation through a medium can be used to estimate the concentration of a compound with a known absorption coefficient in a transparent mixture. Now let's see one of the applications of emission spectroscopy, which is combustion studies. Emission spectroscopy is a powerful tool for studying combustion processes. By analyzing the light emitted from a flame, researchers can gain valuable insights into the chemical composition, temperature, and reaction kinetics of combustion processes. The different ways in which emission spectroscopy is used include the identification of reactive species.

Emission Spectroscopy – Combustion studies



- Emission spectroscopy is a powerful tool for studying combustion processes.
 - By analyzing the light emitted from a flame, researchers can gain valuable insights into the chemical composition, temperature, and reaction kinetics of the combustion process.
- 1. Identification of Reactive Species** – Radical and intermediate species detection during combustion reaction pathways. Also, the intensity of spectral lines emitted by species in the flame is directly related to concentration emitting atoms.
 - 2. Combustion Efficiency:** The presence of different product species can be known using emission spectrum which determine the combustion efficiency.
 - 3. Pollutant Formation:** Emission spectroscopy can be used to monitor the formation of nitrogen oxides (NO_x), soot and other major air pollutants.
 - 4. Flame Structure and Dynamics:** Visualizing spatial and temporal flame dynamics and distribution of species.

Emission Spectroscopy – Combustion studies



Experimental Techniques:

- **Optical Emission Spectroscopy (OES):** Measures the intensity of light emitted by excited species introduced into a flame.
- **Laser-Induced Fluorescence (LIF):** Uses laser excitation to selectively excite specific species and measure their fluorescence.
- **Planar Laser-Induced Fluorescence (PLIF):** Provides 2D images of species distributions within the flame.
- **Chemiluminescence:** Measures the intensity of the light emitted by the excited species formed during a chemical reaction during combustion in a flame.

By employing these techniques, researchers can gain a deeper understanding of combustion processes, optimize engine performance, and develop cleaner and more efficient combustion technologies. Using these visualization techniques in the flame diagnostics to obtain:

Spatially Resolution: Visualizing the spatial distribution of different species within the flame.

Temporal Resolution: Time-resolved spectroscopy that can capture the rapid changes in the flame structure and chemistry.

which are radicals and intermediate species that occur during the reaction pathways in combustion. Also, the intensity of the spectral lines emitted by these species in the flame is directly related to the concentration of the emitting atoms. Next, this also helps in determining the combustion efficiency by studying the presence of different product species using the emission spectrum of the product gases. Next, emission spectroscopy can also be used to monitor the formation of nitrogen oxides, NO_x emissions, soot, and other pollutants. The study of flame structure, flame dynamics, and visualization will

give us information about the distribution of species, the flame front location, and flame heat release dynamics, which will help us optimize the combustors.

Now let's see the different experimental techniques that are used in combustion studies, which are based on spectroscopy. The first one is optical emission spectroscopy. In this technique, the species that has to be studied is introduced into a flame, and the light emitted by the species after getting excited using the flame is measured. The other kind of technique is LIF. Here, laser is used to excite specific species inside the flame, and their fluorescence is measured.

Extension of this technique, which is planar laser induced fluorescence, is a technique that provides 2D images of species distributed within a flame; for this, a laser sheet is used, which is created using sheet-making optics. Another technique that is important in combustion studies is chemiluminescence. As explained before, chemiluminescence occurs when light is emitted by a substance due to the energy. Generated during chemical reactions in combustion studies, specifically during combustion due to chemical reactions that are exothermic in nature, that energy is used by the intermediate species, which get excited to higher energy states, and when they de-excite to lower energy states, they emit radiation at specific wavelengths. The measure of the intensity of light emitted by these excited species formed during the chemical reaction during combustion is chemiluminescence.

By employing such techniques, the researchers can gain a deeper understanding of combustion processes, optimize engine performance, and develop cleaner and more efficient combustion technologies. Using these visualization techniques, we can obtain spatial resolution for visualizing the spatial distribution of different species within the flame and temporal resolution through time-resolved spectroscopy, which can capture the rapid changes in the flame structure and chemistry. So chemiluminescence spectroscopy is similar to atomic spectroscopy, which uses quantitative measurements of optical emission from excited chemical species to determine concentration. The primary difference is that it measures emissions from energized molecules during a chemical reaction instead of simply excited atoms. The spectra obtained by this technique emanate from molecular emissions, which are broader and more complex bands.

The chemiluminescence can take place either in solution or gas phase, whereas atomic emission spectroscopy is almost strictly a gas phase phenomenon. The chemiluminescence, by its name, suggests that the light is generated from chemical energy and does not come from an external lamp. Thus, the problem of scattering the radiation from the excitation source is completely avoided, as there is no external lamp or laser used in chemiluminescence. Next, let's see specifically how chemiluminescence

occurs in terms of chemical reactions. In chemiluminescence, the luminescence, or the generation of light, is due to a chemical reaction, as explained before.

Chemiluminescence Spectroscopy



- **Chemiluminescence spectroscopy** is similar to atomic spectroscopy which uses quantitative measurements of the optical emission from excited chemical species to determine concentration.
- Primary difference is that it measures the emissions from the energized molecules (during chemical reaction) instead of simply excited atoms.
- The spectra obtained by this technique emanate from molecular emissions – broader and complex bands.
- Chemiluminescence can take place either in solution or gas phase, whereas AES is almost strictly a gas phase phenomenon.
- The chemiluminescence by its name suggests that the light is generated from chemical energy and does not come out from external lamp.
- Thus, the problem of the scattering of the radiation from the excitation source is completely avoided, as there is no external lamp or laser used.

Chemiluminescence



- In Chemiluminescence, the luminescence (generation of light emission) is due to a chemical reaction.



- For achieving Chemiluminescence, the exothermic reactions have to generate energy sufficient to excite electrons from ground state to excited state.
- In general, Exothermic oxidation reactions \rightarrow Chemiluminescence.
- The following reaction shows that an intermediate radical (C^*) is formed which is in electronically excited state, which may subsequently relax to ground state by emitting photon.



Here, as we can see, reactants A and B combine to form products, and they produce light. To achieve chemiluminescence, the exothermic reaction must generate sufficient energy to excite electrons from the ground state to the excited state. This is an important criterion. So, in general, exothermic oxidation reactions are capable of producing

chemiluminescence. So, to be precise, the following reaction shows the intermediate radical c^* which is formed in the products, that is, in an electronically excited state, which may subsequently relax to the ground state by emitting a photon.

So, when the reactants a and b combine, they form an intermediate species c^* , which is unstable and in an excited state. Now, this c^* . Radical de-excites to the ground state, emitting light; this is what happens during chemiluminescence in combustion reactions. As explained before, depending on the energy difference between the excited state and the ground state of this specific species, the energy of the photon is dependent, which determines the wavelength at which the light emission occurs. Thus, by isolating and allowing only a specific wavelength into the camera using a specific bandpass filter at that wavelength, we can measure chemiluminescence at that wavelength and obtain the spatial distribution of that species inside the flame.