Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of $250 for UW-Madison chemistry Ph.D. candidates.

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The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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Quantitative Temperature & Formaldehyde Concentration Imaging for High-Pressure Turbulent Fuel Jet Ignition

By

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Overview for Non-Scientists

I have written this chapter of my thesis to communicate my research with as wide of an audience as possible, and not just scientists. Scientific research should be conducted to benefit all of society; as such it is imperative that scientists communicate their findings with others. Scientific communication is especially important as scientific research becomes more specialized, and the communication barrier between the sciences and the humanities [1] remains or even grows. Naturally, the inability to communicate is a significant challenge to overcome in solving the various problems of the world. Communication is all the more important when political and economic decisions are being made in response to questions that are inherently scientific, in particular those regarding climate change and energy policy. Thanks to the Wisconsin Initiative for Science Literacy (WISL) at UW-Madison for the opportunity and platform to present my research to a non-science audience, and for sponsoring and supporting the creation of this chapter.

1.1 Introduction

Climate change is widely recognized by scientists and non-scientists alike as one of the most important challenges for our generation. The American Physical Society (APS) has even released the following statement in 2007 [2]:

> The evidence is incontrovertible: Global warming is occurring.
>
> If no mitigating actions are taken, significant disruptions in the Earth's physical and ecological systems, social systems, security and human health are likely to occur. We must reduce emissions of greenhouse gases beginning now.

To provide some context for this statement, scientists, let alone major scientific associations, rarely if ever make direct statements like this. Scientific writing typically leaves room for the unknown; scientists understand that no measurement is perfect, and that there is always room for error. That makes the APS' statement all the more significant: even in 2007, scientists accepted human causes of global warming as an indisputable fact. Our understanding of human impacts on climate change has evolved significantly since then, and in 2018 scientists for the first time identified extreme weather events that could only have occurred as a result of human influences on climate change [3]. Clearly, the problem of global warming and climate change is significant, and we're already seeing some of its initial impacts.

Global warming is a problem, but what do we do about it? To answer that, we need to know something about its causes. Global warming is usually described as the result of greenhouse gases, which trap infrared light that would otherwise escape Earth's atmosphere. The trapped radiation is ultimately absorbed again at the Earth's surface, heating the planet. A major source of greenhouse gases is combustion engines, which in the US produce around 30% of greenhouse gas emissions. Combustion engines are used in our cars and trucks, in planes, in power plants, and in industrial settings for a wide variety of tasks; they are even used to power recreational equipment like jet skis and snowmobiles. It has been suggested by combustion scientists that we can potentially reduce greenhouse gas emissions from combustion engines by 50% [4] simply by improving fuel efficiency, potentially going a long way toward reducing the impacts of climate change. Development of other technologies could decrease emissions even further.

Unfortunately, we can't just stop using combustion engines. Much of our economy, food and water supply, and essential services rely on combustion engines; alternatives do not exist (and may not for many years) that can act as a drop-in replacement. Instead, it is important that we continue to work on improving the technology that we do have as one step towards reducing carbon emissions. Unfortunately, scientists do not have a good understanding of much of the chemistry and physics that drives engine performance and emissions formation. Developing this understanding is critical for making better engines, and for shifting to more advanced engine designs or fuels. My research over the past 6 years has focused on developing tools that allow scientists to understand what is happening inside engines. The specific tools I develop are called optical diagnostics, which largely employ cameras and lasers to make measurements inside engines. Advanced optical diagnostics let us capture an immense amount of information in a very short time that is not accessible in traditional experiments. For the remainder of this chapter, I will discuss my contribution to the development of optical diagnostics for combustion engines. In particular, my research focuses not only on development of specific tools, but also aims to answer the question how do I choose or design a tool for a specific combustion experiment. I'll start with a short motivation for my work, and discuss why better tools are needed. Next, I'll provide a brief description of the optical diagnostics I've been working on these past six years. Then, I'll discuss some background information that is important to diagnostics, namely quantum mechanics, and outline some of our research results that specifically focus on the physics of optical diagnostics. Finally, I'll discuss some specifics of engines, and how we design diagnostics to make measurements in engines.

1.2 Global Warming & Other Impacts of Carbon Emissions

Before jumping into the specifics of my research, I want to outline some of the physics involved in global warming. Global warming serves as both the very high-level personal motivation for my work in combustion, but also is an excellent example of some of the physical concepts that come into play for optical diagnostics. In fact, the diagnostics I've spent my academic career developing and designing operate on the same principle by which the Earth is heated: absorption and emission of radiation. The remainder of this section contains a brief overview of global warming; a more complete description with many additional details is provided by the American Chemical Society in their climate science toolkit [5].

Temperature is a measure of how much energy an object has stored; as an object absorbs more energy, its temperature will increase. When we think about the temperature of an object, say the Earth, what we're really interested in is the energy balance: where does energy come from, and where does it go? If we consider Earth as a whole, the vast majority of energy available on Earth comes from the Sun. The Sun itself is a large hot ball of gas, mostly hydrogen. Since the Sun is so hot, it behaves similar to an incandescent light bulb: it radiates a significant amount of heat in addition to light. The Earth is a large nearly spherical rock with a thin atmosphere surrounding it. A small portion of the radiation emitted from the Sun reaches Earth and can be absorbed (heating the Earth), or reflected. Even though the Earth is very cold compared to the Sun, the Earth will also emit radiation; this is how Earth maintains its temperature. A diagram of the Earth-Sun system is shown in Figure 1.1 with some of these processes shown schematically. All of these competing processes collectively determine the temperature of Earth.

If Earth had no atmosphere, the average surface temperature would be around 0°F. But, as it stands, only around 60% of energy emitted from Earth escapes, and the surface temperature on average is closer to 60°F. This is a result of the greenhouse effect. A large portion of the radiation emitted from Earth is absorbed by the greenhouse gases and clouds in the atmosphere and ultimately emitted back towards the Earth. Much of the re-emitted radiation is absorbed at Earth's surface, increasing the planet's temperature. As we add more greenhouse gases to the atmosphere, less radiation escapes (*i.e.*, more radiation is reabsorbed at Earth's surface), further increasing the temperature. As Earth warms, the problem gets worse: the polar ice caps slowly melt reducing Earth's ability to reflect Solar radiation. The warmer Earth also raises the temperature of the atmosphere, allowing it to hold more water vapor

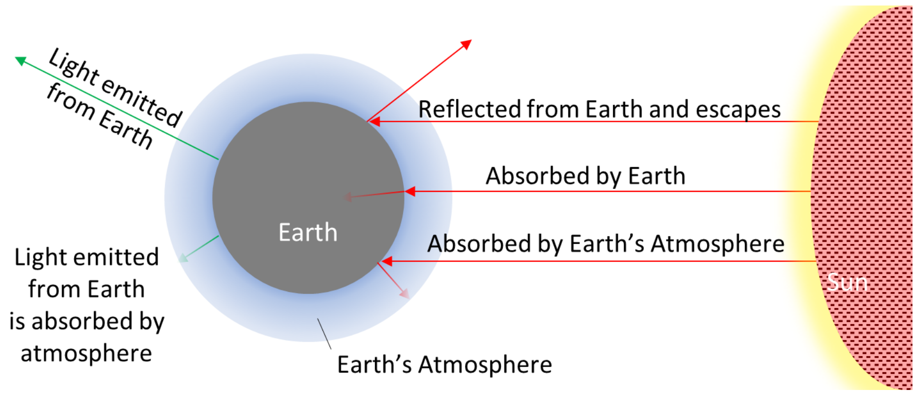

Figure 1.1: Diagram of Earth-Sun system showing the different paths radiation can take as arrows.

(water vapor being the largest contributor to the greenhouse effect). There are also changes that can act to decrease the greenhouse effect as Earth warms, like the formation of more clouds (resulting from the additional water vapor) that reflect Solar radiation. However, in total, the greenhouse effect tends to become more severe at higher temperatures, and changes in carbon dioxide emissions tend to have a large impact.

The IPCC estimates that doubling the amount of carbon dioxide in the atmosphere will increase Earth's surface temperature by an additional 3-8°F . This may not seem like a significant change; Madison, WI experiences typical temperature swings from 40 to 60°F routinely each day in Spring. It's really important, however, to realize what this temperature increase really means. Imagine having a cup of boiling water in one hand, and a small ice cube in the other. The average temperature of these two objects (*i.e.*, the temperature of the water if I were to put the ice cube in and let it melt) is relatively high, say 195°F. If I replace the ice cube with liquid water at the same temperature, the average temperature of the two objects increases to around 200°F. By replacing ice with liquid water, the average temperature of the system increases by only 5°F, and the temperature of the two individual objects hasn't changed, but we obviously no longer have any ice. This is illustrated in Figure 1.2. On Earth, a primary effect of global warming is to shrink the polar regions in much the same way that the ice cube melts and is replaced with liquid water in our example. The slight temperature increase is only a symptom of a larger issue: the balance between cold and hot regions on the planet is disrupted, particularly in the form of melting polar ice caps and shrinking regions of cold polar air. Smaller polar air regions tend to be less stable and move more frequently to lower latitudes, leading to more extreme weather events. Beyond this, increased greenhouse gas concentrations in the atmosphere already are having significant impacts on temperature, ocean acidity, and rising sea levels, all of which can have profound impacts on human and natural systems.

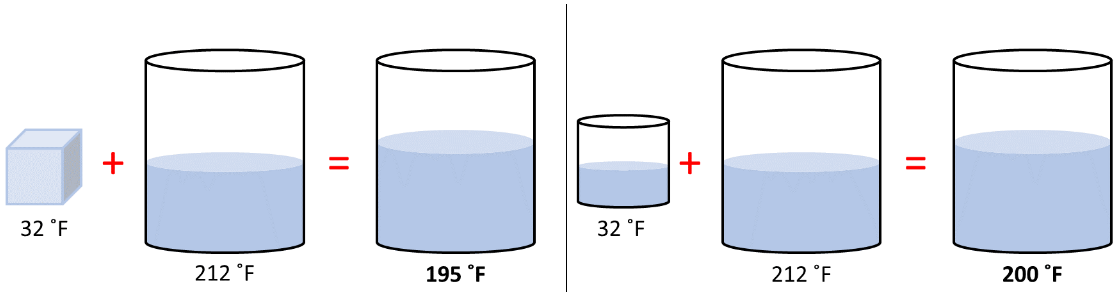

Figure 1.2: Illustration of water and ice mixing. Left: an ice cube is added to a cup of boiling water, which melts, resulting in an average temperature of 195°F. Right: liquid water (with the same initial temperature) is added instead of ice, resulting in an average temperature of 200°F.

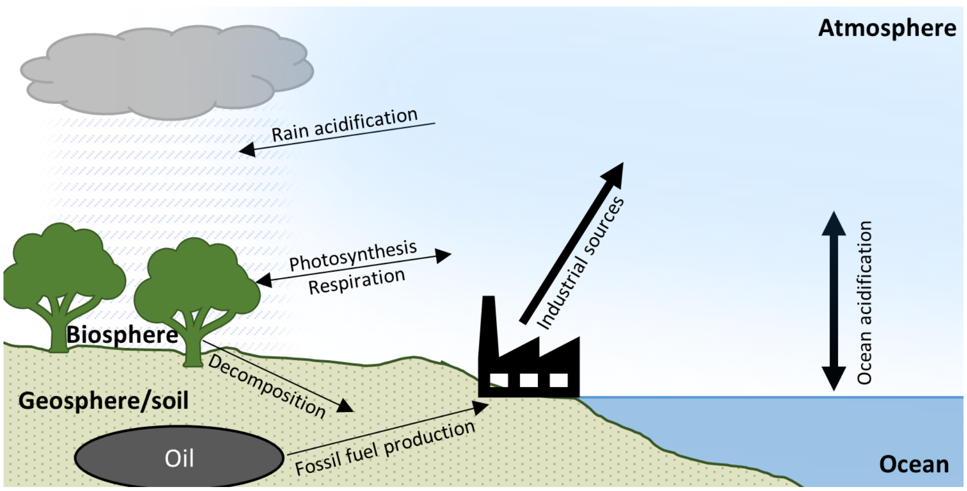

Figure 1.3: Illustration of a portion of the atmospheric carbon cycle showing several of the ways carbon enters and exits our atmosphere. Some important processes are not drawn, including interaction with Earth's geosphere (*i.e.*, soil) and other human sources (*e.g.*, agriculture).

Figure 1.3 shows a simple diagram of Earth's atmospheric carbon cycle, which shows some of the ways carbon is stored on Earth. From the diagram, burning fossil fuels adds carbon to the atmosphere which can eventually move into the ocean, into the soil, or into plant matter. Burning any fuel adds carbon to the atmosphere, but fossil fuels specifically add "old" carbon, or carbon that has been stored underground for millions of years. Since it takes millions of years for plant matter to decompose into oil again, "old" carbon is not "recycled" back to its original state, and adds more carbon overall. With new technologies, we focus on "renewable" fuels where the carbon is recycled back to its original state, and only briefly affects the environment as the carbon moves from the atmosphere into the biosphere (or plant matter) again. We also hope to develop improved engines that are more efficient, so less carbon is released overall. In both cases, scientists need better tools to understand the chemistry and physics that happens inside engines.

Internal combustion engines (like those used in cars and trucks) have been around for over a hundred years; one may naively assume we know everything there is to know about combustion, but this is far from the truth. Early engines were developed from the simple understanding that a fuel burns after it is compressed and heated. In fact, we are still very far from having a thorough understanding of the physics and chemistry at play; scientists are only recently beginning to understand the coupled physics and chemistry of the fuel and air mixture inside an engine. This understanding is becoming more critical to engine design now because we're interested in increasing efficiency and using alternative "carbon neutral" fuels to fight climate change. Alternative fuels can behave very differently from more traditional fuels like gasoline and diesel; we need to understand the physics and chemistry at play to be able to use alternative fuels effectively. We also need this understanding to make engines more efficient. Every gallon of gasoline contains around 5 pounds of carbon, and burning a gallon of gasoline produces about 18 pounds of carbon dioxide gas. Developing tools and performing experiments to learn about the detailed physics and chemistry of combustion in engines is necessary to make more efficient engines (ultimately burning less fuel), and to design engines to better use alternative fuels.

1.3 Optical Diagnostics & Aerosol Phosphor Thermometry

The discussion of global warming in the previous section not only describes my motivation for studying combustion, but also serves as an excellent example of how light and matter interact. In that discussion, the Sun, since it is very hot, emits radiation in the form of heat and light. The Earth absorbs and reflects some of that radiation. Greenhouse gases in the atmosphere absorb a small fraction of the radiation as well. This is the same principle on which optical diagnostics operate. Using optical diagnostics, we aim to measure temperature or other parameters by exciting an object (*e.g.*, by shining a light on it until it absorbs light), and measuring the light that comes out with a camera. This process of light absorption and emission is illustrated in Figure 1.4. Imagine shining a flashlight into a box with a cloud of particles. The light is initially white, meaning it is composed of all colors with equal brightness. If the particles are luminescent, meaning they can absorb and emit light, particles will absorb some of this light, but only certain colors are absorbed. The remaining light passes through the particles. After the particles absorb some light, they can re-emit with a different color. Usually the emitted light is red-shifted, meaning the emitted light contains more red light than the absorbed light.

The technique we're interested in here is called laser-induced fluorescence. Laser-induced means that we're using a laser to provide light for our particles to absorb, and fluorescence is the scientific term for light that is emitted from a molecule quickly. This is identical to how glow-in-the-dark toys work. Imagine a glow-in-the-dark ball. The ball is initially outside during the day and absorbs light from the

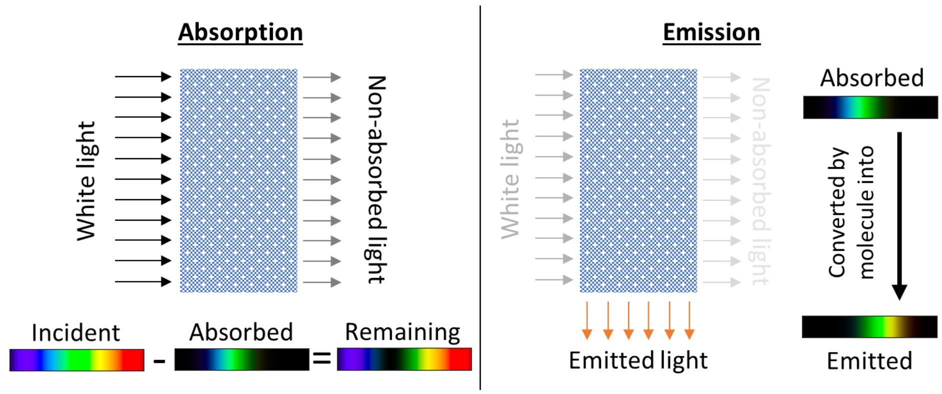

Figure 1.4: Illustration of white light interacting with an absorbing material. Only certain frequencies (colors) of light are absorbed and the rest are unaffected. The material later emits light at a different frequency. Note the emitted light is "red-shifted" with respect to the absorbed light.

Sun. Then, moving it indoors into a dark room, the ball glows dimly as it re-emits some of the light it absorbed earlier. For optical diagnostics, we replace the Sun with a laser, and instead of toys we are looking at molecules or tracer particles smaller than a grain of sand. (We call them tracer particles because they are meant to trace the motion of the fluid flow.) The molecules or particles we're interested in also re-emit the light they absorbed over a very small fraction of a second (less than 1 millionth of a second typically), while glow-in-the-dark toys emit lightly slowly over hours.

Over the last six years, I have worked to improve our understanding of the physics of these tracer particles so we can make better optical diagnostic tools for engines. This work has focused on trying to answer the following questions:

- How does temperature affect how a molecule or particle absorbs and emits light?
- What parameters are important for designing or choosing a particular optical diagnostic tool?
- Can we predict how well an optical diagnostic will work?

The last bullet point is perhaps the most important. Not only do we need to develop these experimental techniques, but we really need to understand how well they work. Every experiment and every measurement has some error or uncertainty associated with it. To design or choose an experimental method we need to know what this uncertainty or error is, and we need to know whether a tool is capable of answering our scientific questions.

The questions posed above are very broad. In my thesis, I focus on a specific subset of the problem, where I investigate solid tracer particles called thermographic phosphors (thermographic meaning that some properties change as temperature changes, and phosphor meaning the particles can absorb and emit light), and focus on the design of a temperature measurement tool for the air and fuel mixture

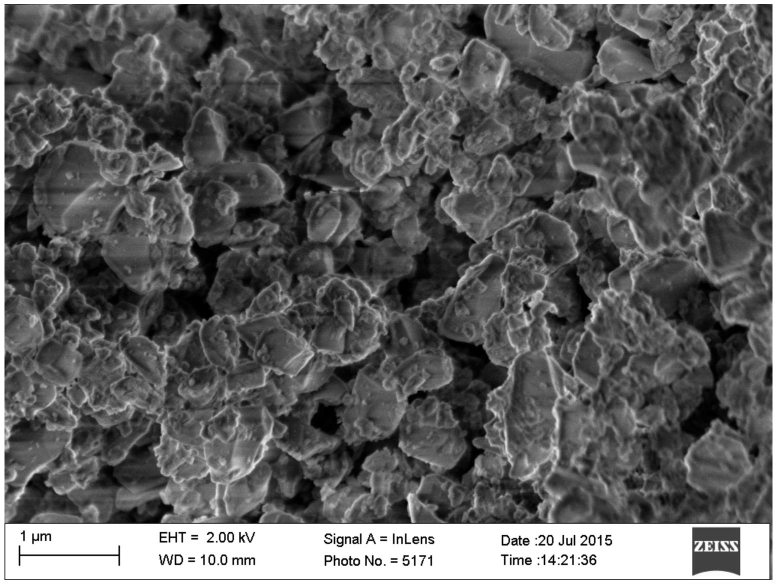

Figure 1.5: Scanning electron microscope image of a phosphor sample

inside of a diesel engine just before the fuel ignites. The technique of using thermographic phosphor particles to measure gas temperatures is called aerosol phosphor thermometry. In practice, we put these phosphor particles into the engine suspended in air (similar to how dust can be suspended in air) and we shine a laser on them. Similar to the glow-in-the-dark ball or the Earth, the particles absorb some of the laser light and reflect some of it. The light that is absorbed is later emitted again with a different color, and we observe and measure the emitted light by taking pictures with scientific cameras. By looking at the color (or frequency) of the emitted light, and the brightness of the emitted light, we can determine the temperature of the particle.

The particles themselves are very small, usually less than a micrometer in diameter (1 thousand micrometers is equal to a millimeter); a microscope image of a phosphor sample is shown in Figure 1.5. The particles in this image are made of a garnet (similar, but not identical to the gemstone garnet), but some of the atoms are pulled out and replaced with praseodymium ions. The praseodymium ions are what gives the particle its ability to absorb and emit light. This is only one example though; many different materials (and ions) can be used to make a phosphor, and a major challenge of this work is to find the best material for a given experiment.

1.4 Quantum Mechanics and Phosphor Photophysics

We aim to measure temperature with these tracer molecules or particles by taking advantage of their absorption and emission properties. What does temperature have to do with absorption and emission

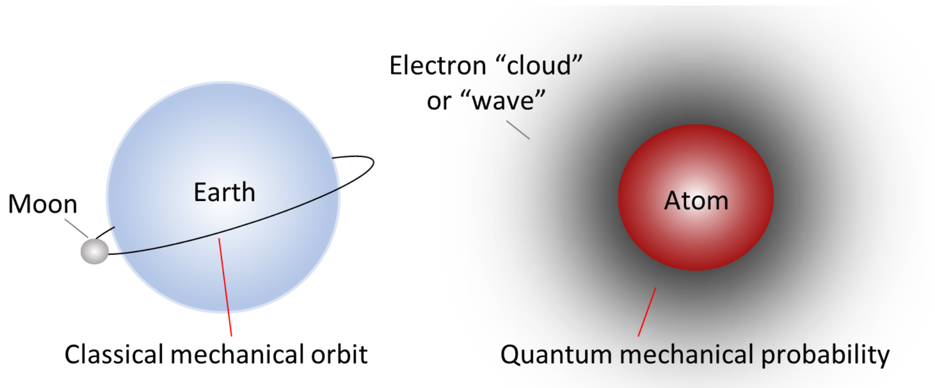

Figure 1.6: Illustration of the Moon orbiting Earth (left) and an electron orbiting an atom (right). The dark cloud or fog surrounding the atom indicates the likelihood of an electron being at that location. Near the center of the atom, the cloud is very dark and dense, indicating electrons are more likely to be near the center.

of light? To answer this question, we need to delve into the field of physics that describes the atom: quantum mechanics. You might be wondering, what does quantum mechanics have to do with combustion measurements? Quantum mechanics is the theory that describes what happens when light interacts with matter.

More specifically, quantum mechanics is the theory that describes how matter (including electrons and atoms or molecules) interact at very small scales (at distances around a billionth of a meter). In popular science, quantum mechanics typically evokes images of a thought experiment by Erwin Schrodinger about a cat in a box that may or may not be dead. Schrodinger suggests that the cat is both dead and alive (the cat's life being controlled by an atomic process), and that the ambiguity is only resolved when one 'measures' or observes the cat. From a practical standpoint, this can be misleading. This would imply quantum mechanics is a theory about what we don't (or can't) know or understand. A more approachable and useful description is that quantum mechanics is a theory of probability; it tells us how likely certain events are. This is a key part of the Copenhagen interpretation of quantum mechanics. In this interpretation Schrodinger's thought experiment does not pose a problem; the outcome is determined long before a conscious observer opens the box, with both outcomes equally likely.

Quantum mechanics, however, cannot tell us what will happen, only what may happen. As an example, consider the Moon orbiting Earth. Classical mechanics can tell us the precise path that the Moon will take around Earth. An electron orbits an atom in much the same way (mathematically speaking), but quantum mechanics cannot tell us the electron's precise path. Instead, it tells us the probability with which the electron will be at any given location. This comparison is shown in Figure 1.6. This feature makes quantum mechanics unintuitive, even to experts in the field.

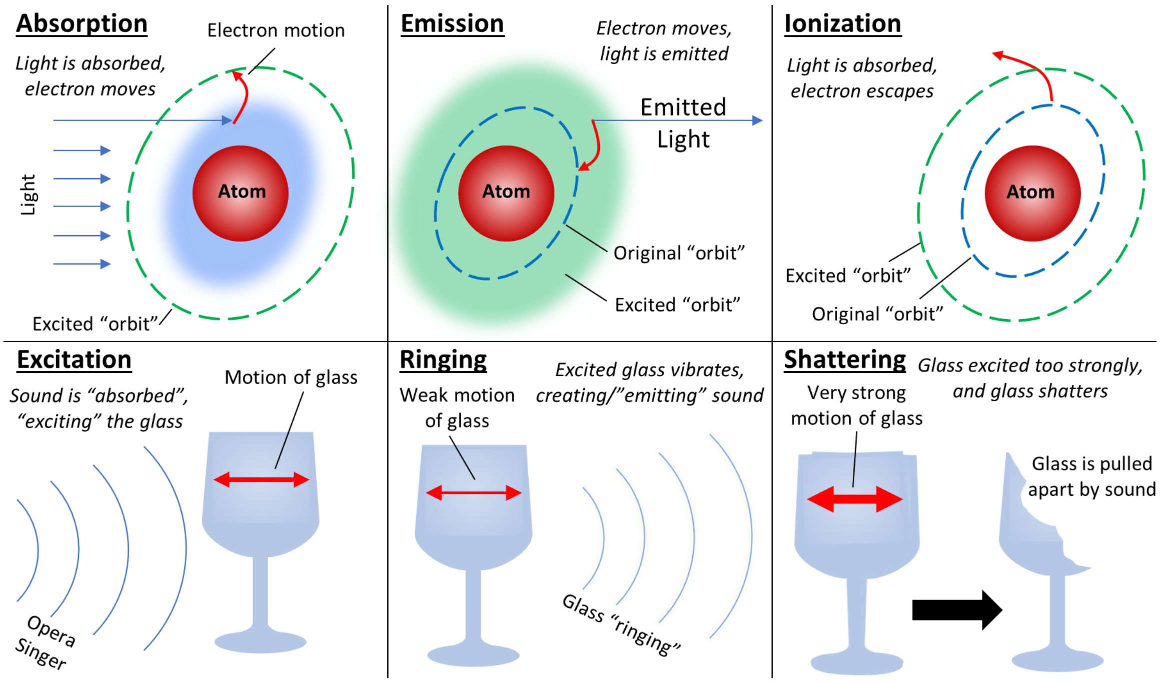

Figure 1.7: Illustration of absorption and emission of light by an atom (top) in comparison with the excitation of a wine glass by an opera singer's voice (bottom). Red arrows indicate the motion of electrons (in the case of the atom) and the glass (for the wine glass example). Electrons are shown as shaded blue or green clouds around the atom, and the empty orbits are shown as dashed curves.

Besides telling us something about how electrons orbit atoms, quantum mechanics is necessary to understand the details of optical diagnostics, and especially how objects absorb and emit light. If we consider again an electron orbiting an atom, this system can absorb light. Light, being a wave, pushes on the electron in orbit. If the light has the appropriate frequency (or color), making it resonant with the electron, the electron can be pushed into a different orbit (similar to how an opera singer can cause a glass to vibrate by singing at the glass' resonant frequency). This pulls some energy out of the light field, and gives it to the electron. Emission, or the "glow" in glow-in-the-dark, is the reverse process; after the opera singer stops singing, the glass still "rings", producing sound. Similarly, after absorbing light and moving to a new orbit, an electron will fall back down to its original orbit and in doing so will create a small burst of light. Each of these processes (absorption and emission of light, as well as the resonating glass) are illustrated in Figure 1.7. As an aside, if the frequency of light is too high, the electron can actually be ripped away from the atom, similar to how an opera singer can shatter a glass by singing loudly at the glass' resonant frequency. This is of course not desirable, because light cannot be emitted if the electron is ripped away from the atom, as a broken glass cannot produce sound.

As I mentioned, quantum mechanics is a theory of probability. To make a diagnostic, we need to know the probability that a molecule or phosphor particle will absorb light, and the probability that it

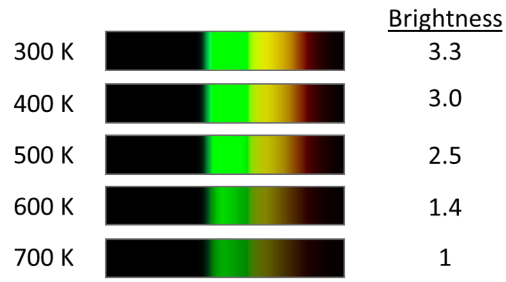

Figure 1.8: Color content and brightness of a phosphor sample as it is heated from room temperature (300 K) to 700 K (or 800°F). The "brightness" value next to each panel measures the relative brightness of the emission, compared to the value at 700 K. For example, the phosphor is 3.3 times brighter at room temperature than it is at 700 K.

will re-emit that light. But why am I discussing probabilities? If we're trying to make measurements, don't we need to know more than just a probability that a particle will emit light? The answer is statistics. Statistics provides a link between the quantum mechanics (the physics of a single atom) and the behaviors we observe in real life (composed of many, many atoms). When we have a large number of atoms absorbing and emitting light, the law of large numbers effectively says we can interpret the probability as a fraction. Going back to Schrodinger's Cat, if we perform this thought experiment 1 million times, statistics would tell us to expect to get each result one half million times.

1.4.1 Phosphor Emission Probability

Let's go back to the question of the probability of absorbing and emitting light. More specifically, we're interested in understanding the photophysics (or the luminescent properties) of different phosphor materials. We can gain some insight into these questions through some simple experiments where we heat a sample of phosphor particles (remember, a phosphor particle is a small piece of material, like a grain of sand, that can absorb and emit light) to a known temperature, excite it with a laser, and measure the color and intensity (brightness) of their emission. The brightness is a measure of the probability with which a phosphor will absorb and emit light. A series of panels showing the color content and brightness of the emission for a phosphor sample at different temperatures is shown in Figure 1.8.

All of the phosphor materials we investigated for thermometry show an interesting trend: the brightness of the emission drops quickly as temperature is increased, but only above some threshold temperature. This suggests that colder particles are more likely to emit light. This phenomenon is called thermal quenching. Imagine our phosphor particle is made up of two billiard balls connected by an elastic band. As we increase the temperature, the billiard balls tend to move faster and pull harder on the elastic band (temperature is a measure of the average speed of the atoms that make up an object). Occasionally the two billiard balls will collide, and the faster they move, the more frequently these collisions will occur. Now, imagine one of the billiard balls absorbs some light and gains some energy. Each collision between the billiard balls provides an opportunity for that extra energy to be transferred to the other billiard ball. Depending on how the energy is transferred, it may not be available to be re-emitted as light. Put simply, after an electron absorbs energy from light, it can either emit a burst of light, or the electron can be pushed back into its original orbit by collisions with other atoms. Since collisions are more likely to occur at higher temperature, less light is emitted as temperature increases. Thermal quenching is the most important mechanism controlling a phosphor's capability for temperature measurement.

Using all of this information, we designed a temperature measurement tool or diagnostic that takes advantage of thermal quenching. We directly measure the brightness of the phosphor particles with a camera, and using our knowledge of the phosphor's thermal quenching, we can find the temperature of the phosphor particle. Since thermal quenching only happens above a threshold temperature, we can only use this technique above that threshold temperature.

Thermal quenching is a double-edged sword. As every photographer knows, the darker an object is, the more difficult it is to photograph, and the noisier or grainier the images tend to be. This makes it more difficult to measure temperature; we need the phosphor to be dim at high temperatures, but it also must be bright enough that we can get a good photograph. Thermal quenching is a property of the phosphor material, so our only option is to find materials with an appropriate threshold temperature. The threshold temperature sets the temperature range where we can make measurements. One additional significant outcome of this work is the identification of several phosphor materials that can be used from around 1350-2250°F, hundreds of degrees hotter than any other aerosol phosphor thermometry measurement has been made.

1.4.2 Particle Absorption Probability

So far, I've mostly discussed the physics of light emission and how it affects our temperature measurements. Absorption of light is an important part of the process as well. A phosphor can only emit as much light as it has absorbed, so if we want a phosphor to be bright (which is required to make a good measurement) we need the phosphor to be able to absorb light with high probability. The probability of an electron absorbing light depends on the frequency of the light. The closer the light frequency is to the resonant frequency, the higher the probability of absorption, just like the opera singer and the glass.

What exactly is resonance though, and why does this matter? When talking about structures (the wine glass, for example), every object has a natural resonant frequency at which it tends to vibrate (for

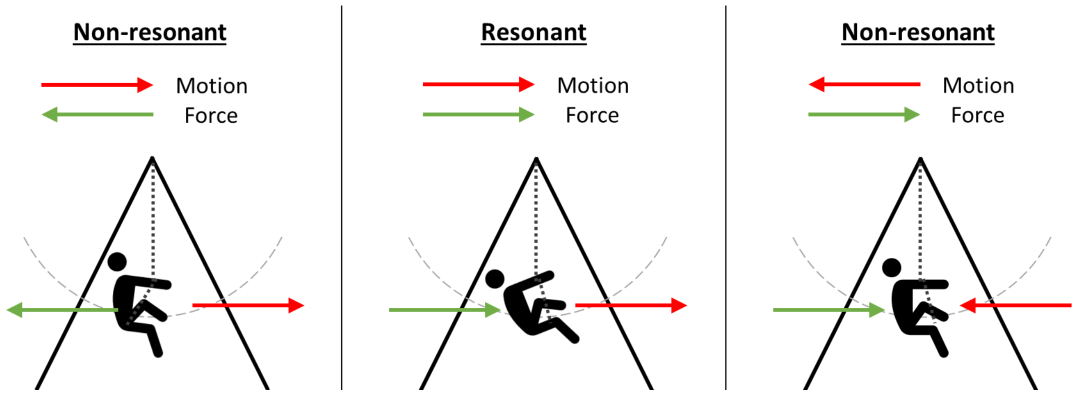

Figure 1.9: Illustration of person on a swing. On the left and right, the person is moving forward, but pushing against the motion, and is non-resonant. In the middle, the person pushes with the motion of the swing, causing resonance.

the wine glass, it's typically around 500-1,000 Hz, or roughly between the musical notes B_4 and B_5). For example, a pendulum on a clock has a natural frequency of 1 revolution per second; this allows it to precisely count seconds – every revolution of the pendulum marks another second passed. If we push on an object at the same frequency, the object will tend to move faster and faster – *i.e.*, the motion caused by pushing an object at its natural frequency is amplified. This amplification is called resonance. As an example, imagine sitting on a swing. If you push forward while the swing is moving forward, you start to swing faster and higher. If you push against the swing, or push at the wrong time, you tend to slow down. Pushing only during the forward motion of the swing is equivalent to exciting the swing at its natural frequency. This is illustrated in Figure 1.9; pushing with the motion of the swing causes resonance and an amplification of the motion, while pushing against the swing does not.

Molecules behave in much the same way. The resonant frequency of a molecule depends on how the electrons are arranged around its constituent atoms (*i.e.*, the shape of electron cloud around the atom in Figure 1.7), just as the resonant frequency of the wine glass depends on the glass' shape, and the resonance frequency of the swing depends on the chain length. When a molecule is excited near its resonant frequency, the electrons are able to move much more quickly – the effect of the laser is amplified when it is resonant with the molecule. Since the electrons are able to interact with the laser more efficiently, the probability with which the phosphor absorbs light increases near the resonant frequency.

In this work we showed that we can make better temperature measurements by using lasers with frequencies closer to the resonant frequency of the phosphor. Using lasers close to the resonant frequency of the phosphor greatly increases the probability that the phosphor will absorb light, which in turn makes the phosphor's emission brighter. We also were able to estimate how the absorption probability changes with temperature for a few different phosphor materials, and have started looking into how temperature influences the phosphor's resonant frequency.

In addition to frequency, several other factors can affect the probability with which a phosphor particle can absorb light. These factors include how bright the laser light is and how long the particles are exposed to the light. Using quantum mechanics and statistics, I developed a model describing how these two factors influence the probability with which light is absorbed. There are a couple conclusions we form from the model. First, perhaps counter-intuitively, the brighter the light is, the lower the probability with which it is absorbed. We generally call this process a non-linear excitation. Similar to how an opera singer shatters a glass, a laser can excite a system so strongly that the electron is pulled entirely out of the system. Once the electron is pulled out, it is not able to emit light so it doesn't contribute to measurement. The second conclusion is that exposing particles to light for a longer period is advantageous. We want to supply a specific amount of light to a particle. If we apply that light very quickly, the particle will see a very bright flash. If we apply the same amount of light over a longer period, the flash will be weaker. Since the phosphors exhibit non-linear excitation, the weaker flash allows the particles to absorb more light. To summarize, a large portion of my work was dedicated to understanding the physics of phosphors, which relies strongly on quantum mechanics. In this section, I've outlined some of the basics of the theories, and discussed what we learned.

1.5 The Combustion Environment & Designing a Diagnostic

The tools I'm primarily interested in designing are to be used in engines. We fill the engine with a cloud of tiny phosphor particles, and replace some of the metal engine parts with glass. With this configuration, we can shine a laser into the engine, and place a camera on the other side to photograph the particles as they "glow". A diagram of the engine pieces, along with a picture of the optical-engine piston and head is shown in Figure 1.10. Relative to the diagram, the camera would be pointing up into the piston window, looking at the fuel jet.

The diagram shows a small box with a diffuse-looking cone entering from the left. The cone represents a diesel fuel jet, or a stream of liquid fuel that breaks up into droplets, and then vaporizes. The diesel jet is actually very similar to a garden hose. Normally when you open the valve on a garden hose, you see a stream of liquid. But, if you partially cover the hose exit, that stream transforms into a more diffuse spray. In the latter case, the liquid jet is moving so fast, friction between the water and surrounding air causes the jet to break apart into droplets. For this project, we're interested in looking primarily at the physics and chemistry of this fuel jet.

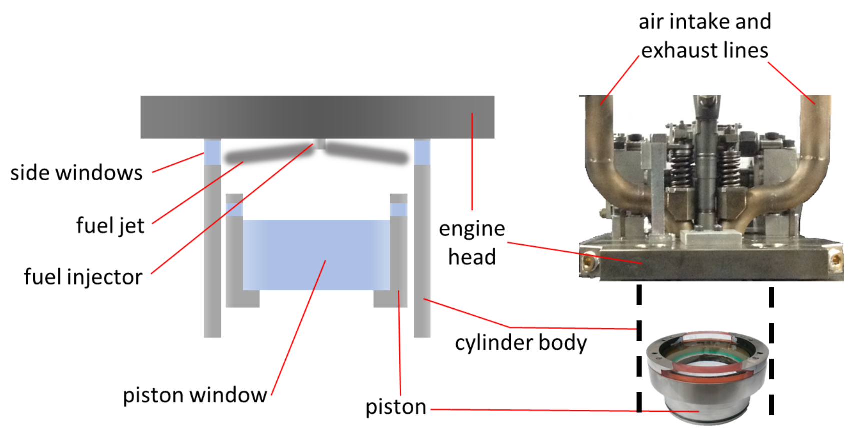

Figure 1.10: Diagram and photograph of optically-accessible engine. The images on the right only show the piston (bottom) and engine head (top), which are featured in the diagram on the left.

The experiment hopefully seems pretty straightforward, but we still have a few questions to answer. Namely:

- How big should the particles be?
- How many particles should we put in the engine?

And of course,

- Which phosphor material should we use?

There are a few secondary questions that are considered in my thesis as well (mostly related to specifics of the laser that is used to excite the phosphor particles) that I won't discuss further here. The last question, which phosphor material should we use, is the hardest question to answer, and for that reason I'll discuss it last.

1.5.1 Particle Size Requirements

Let's consider the first question, how big should the particles be, and try to develop some physical intuition about the problem. There are really two competing issues with particle size. First, the amount of light a particle can emit depends on particle size. When discussing light emission earlier, I talked about electrons absorbing and emitting light. Only the electrons in the particle can absorb or emit light. In fact, only a handful of electrons in a phosphor particle can be resonant with the laser, so only a very small fraction of them can absorb and emit light. By making the particle larger, we're adding more and more electrons, some of which can absorb and emit light. Thus, by increasing the particle size, we can get more light out of the phosphor. Remember, to have a good measurement, we need to have as much light as possible emitted from the phosphor.

The second issue of particle size is slightly more complicated. Imagine a cloud of dust, or even the air in a dusty room. If the air is still, one can see dust particles slowly falling and collecting on the floor. If there is a breeze, one might see the dust particles moving along with the air. Gravity always pulls the particles down, while friction (usually called drag in a fluid) pushes against any motion of the particle. In fact, friction or drag tries to push the particle in the direction the air is moving. If the particle is moving at exactly the same speed and direction the air is moving, there is no drag or friction on the particle.

The particle motion can have a major impact on measurements we make using phosphors. When we use particle-based diagnostics like aerosol phosphor thermometry, we're really measuring the temperature of the particle, not the temperature of the gas. But of course, we really want to know the gas temperature; we need to ensure that the particle is representative of the gas. This means the particle needs to move along with the gas and have the same temperature. We are thus concerned with how quickly a particle responds to a change in temperature or velocity. We can estimate the time it takes for a particle to respond to a change in temperature or velocity; in both cases, the response time increases as particle size increases.

We want to have a large particle to get as much light as possible, but we also need the particle to be small enough to respond quickly to changes in temperature or velocity. The simplest solution is to choose the particle size to be just small enough that they can respond to any changes we expect in the fuel jet. The fuel jet itself is turbulent which, put simply, means that the motion of any individual fuel droplet is random and chaotic. Although this sounds like it should only complicate things, it actually simplifies them: all turbulent jets look alike on average, and scientists know a lot about turbulent jets.

Using this information, I estimate that particles must respond to changes in either velocity or temperature within about 5 microseconds (1 second is equal to 1 million microseconds). If I require a 5 microsecond response time, then the particle diameters must be less than 500 nanometers (1 meter is equal to 1 billion nanometers). Since we want to use the largest particles we can, we should use particles that are 500 nanometers in diameter.

1.5.2 Particle Seeding Density Limits

The second question, how many particles should we use, is a slightly more complicated question. The number of particles we use matters for a couple reasons. When we photograph particles, we never are looking for an individual particle (*i.e.*, we don't see an image of a single sphere). We usually have particles that are so small that they take up less than 1 pixel of the picture. In fact, we may use so many particles that we have 100 or more of them squeezed into a single pixel in the image, so the pictures we take look more like clouds than images of individual particles. We want to have as many particles as we can because every particle we add gives us more emitted light. There are some downsides as well; since we have solid particles suspended in a gas, adding more particles can actually slow down or cool the gas in the engine. This means the particles are intrusive, and could actually change how the diesel fuel jet burns in an unknown way. Having many particles can also impact the quality of our photographs, through a process called multiple scattering. In my thesis I've identified multiple scattering as being the most important factor in determining how many particles should be used.

Multiple scattering (or maybe just scattering) is actually closely related to another popular science discussion, why is the sky blue? As a child I remember seeing this question asked and answered in a public service announcement sponsored in part by Girl Scouts of the United States of America. In the announcement, a young child asks her father why is the sky blue? Dissatisfied with his answer, she answers the question instead. To paraphrase, she states that since blue is the shortest visible wavelength (or highest visible frequency), blue light is diffused by oxygen and nitrogen in Earth's atmosphere up to 10 times more than other colors.

I would alter only one word in her answer: rather than being diffused, I would say light is scattered, meaning that when light strikes a molecule (say, nitrogen or oxygen) it is deflected randomly. Blue light is indeed scattered many times more than red light in Earth's atmosphere. Thus, when we look away from the Sun, we see blue because we're seeing only light that is scattered towards us (most of which is blue light). When looking at the Sun, it appears yellow because we only see light that hasn't been scattered.

We have answered the question why is the sky blue using the concept of scattering. My follow-up question now is why are clouds white? Clouds, similar to air, are made up of particles that scatter light with one significant difference. Air is made up of tiny molecules that do not scatter light very strongly. Clouds, on the other hand, are typically made up of water droplets that are much larger than a molecule. These larger particles are much more likely to scatter light regardless of color; in fact, light will be scattered many times before exiting the cloud again. This is illustrated in Figure 1.11. Since light is randomly scattered so many times, any light that exits the cloud is white.

Multiple scattering can happen in optical diagnostics as well. Instead of clouds of water droplets, we have clouds of phosphor particles that scatter light efficiently. This means that any light emitted inside the engine from phosphor particles can scatter off of other phosphor particles before we can photograph

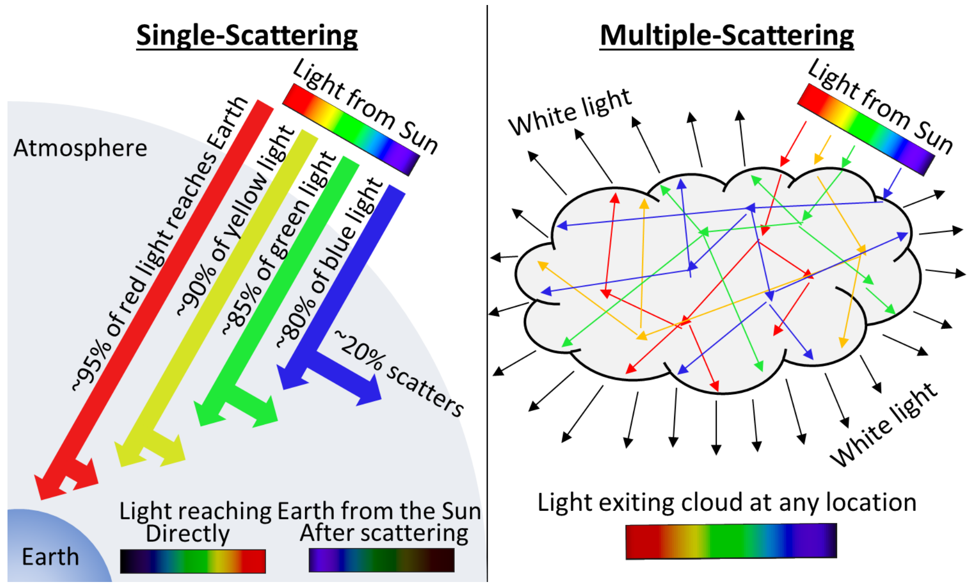

Figure 1.11: Illustration of single scattering in Earth's atmosphere, in contrast with multiple scattering in a cloud.

it. It can also scatter off droplets of liquid fuel. This can make the images appear fuzzy, as though we were taking a photograph of the Sun through a thin cloud or haze. Multiple scattering can also make some regions appear brighter or darker than they should appear, similar to the apparent glow or halo when viewing the Sun through a cloud or haze.

In my thesis I developed a model to estimate how multiple scattering can affect our measurements. It turns out that even for very few particles in the engine, our measurements can be severely impacted. The most important impact is that parts of the phosphor "cloud" appear brighter than they should, similar to how the Sun illuminates an entire cloud, and not just the portion of the cloud that obstructs one's view of the Sun.

There are other impacts from multiple scattering as well. We excite laser particles using a laser beam that is formed into a narrow sheet. Imagine this as a laser pointer where instead of a "dot", the light forms a thin line. Multiple scattering makes this beam spread out, so instead of a thin line, we might see a thick line or even a rectangle. This same effect happens with laser pointers. Although lasers tend to diverge slightly even without multiple scattering (*i.e.*, the "dot" is larger when you are shining the laser from further away), the shape of the laser pointer beam can be distorted when it passes through clouds or even air at long distances.

To avoid large experimental errors, I found that we need to have a relatively small number of particles in the engine. A single pixel in a photograph should have no more than around 50 particles. Although this number may seem large, the particles themselves are very small. In fact, the particles we use here are about 10 times smaller in diameter than the water droplets that make up many clouds (which in turn are about 1,000 times smaller than raindrops).

1.5.3 Precision Requirements and Phosphor Selection

The last question we need to answer in designing an experiment using aerosol phosphor thermometry is which phosphor should I use? To be able to answer that, we need to understand the benefits different phosphor materials can bring to an experiment. Of the materials we've identified, there are two properties that really control how well they can measure temperature: the phosphor brightness, and the phosphor quenching temperature.

From the previous section, thermal quenching is the phenomenon where phosphors emit less light at higher temperatures. We need to have thermal quenching to be able to measure temperature – if the phosphor's brightness doesn't change, we can't determine its temperature. But, if there is too much thermal quenching, the phosphor won't be bright enough to photograph. We want to choose a phosphor that begins to quench at temperatures slightly colder than the temperatures we're trying to measure. In this case, we want to measure at temperatures where diesel fuel starts to burn. This is typically around 800°F at the coldest. We have identified several possible phosphors that have thermal quenching temperatures around 800°F.

Phosphor brightness depends on other things besides thermal quenching. At cold temperatures (room temperature or colder) thermal quenching does not happen at all in most phosphors. Instead, the phosphor's brightness is partially intrinsic to the phosphor, and partially controlled by the laser frequency (or color) used to excite it.

Choosing a phosphor is very difficult because of these complexities. I approach this problem by determining how precise a temperature measurement needs to be, then determining which phosphors are capable of providing that precision.

So how good of a measurement do we need? Diesel ignition is controlled by chemistry. If we have a mixture of air and fuel that is hot enough to burn, chemical reactions will cause the fuel to break apart and combine with oxygen in the air. This chemical reaction releases heat and raises the temperature of the gas. Some mixtures of fuel and air, typical of diesel engines, will actually burn in two steps; one at low-temperature and one at high-temperature. The low-temperature step happens first and heats the gas by about 200°F or less. By considering this temperature increase, I estimate that we need to measure temperature to within 2.5% or about 50°F of its true value. This may sound pretty simple; after all, most digital thermometers can measure within 2°F, and medical grade thermometers even less.

But thermometers are very different devices – a thermometer is large (several millimeters or more in diameter) and measures slowly. It can take several seconds or even minutes to get a measurement. We use thermographic phosphors because we can measure things very fast (within less than a microsecond, or more than 100,000 times faster than the blink of an eye) and in small spaces (phosphor particles are less than a micrometer in diameter, or about 100 times smaller than the thickness of a human hair). Beyond that, we're interested in measuring temperatures at 1700°F or higher, and no traditional thermometer is capable of that.

Now that we know what our temperature precision should be, we predict the temperature precision we can achieve using each of the phosphor materials. This is a mathematically-intensive process, and a large portion of my thesis is dedicated to doing just this. It turns out that several of the phosphors we investigated can meet our criterion, but each at a different range of temperatures. There is no single phosphor that can cover every scenario we'd like to measure.

In this case, we choose phosphor materials by trying to predict how well each material will work for our application, then choosing the one that appears to work best. But this isn't always possible, especially when there are a lot of possible materials to choose from. Instead we rely on more general observations about phosphor performance. Some general observations we've found from this work are:

- Our best performance typically comes from phosphors that are intrinsically bright, or by using lasers with frequencies near the phosphor's resonant frequency
- We are usually only able to measure temperatures slightly hotter than the phosphor's quenching temperature

But perhaps the most important lesson is simply that designing a diagnostic or experiment is not a simple task. Many factors come into play, and many of the aspects of diagnostic performance are coupled to each other.

1.6 Conclusions

Throughout this chapter, I've outlined my work investigating, improving, and designing optical diagnostic methods primarily using aerosol phosphor thermometry. My work focused on understanding the optical properties (or photophysics) of these materials and tried to understand the physics of light absorption and emission in these materials. I discussed this throughout Section 4. The second goal of my work was to outline a framework for experiment design, design a diagnostic using that framework, and estimate the diagnostic's performance. I discussed this in Section 5. Some of the highlights of my work that I discussed or mentioned in this chapter include:

- Characterized several new phosphor materials that could be used for aerosol phosphor thermometry
- Improved our understanding of, and developed a model for, absorption and emission of light in phosphors
- Demonstrated temperature imaging experiments using aerosol phosphor thermometry at over 1500°F in an atmospheric flame
- Characterized the effects of tracer particle response and multiple scattering on diagnostic performance
- Developed a framework for the design of aerosol phosphor thermometry diagnostics
- Developed a performance prediction model for aerosol phosphor thermometry diagnostics
- Designed a diagnostic approach that could be used to investigate ignition in diesel engines

As with any scientific work, new problems and questions arise in the course of conducting research. In this case, I spent a lot of time investigating the impacts of different effects like multiple scattering on the performance of my diagnostic, and I formed conclusions from that analysis. Future work needs to experimentally validate both the models I developed, and the conclusions I formed. Some other things that need to be done in the future include:

- Perform the diagnostic in an engine
- Measure the absorption and emission properties of additional phosphors identified in this work
- Validate the phosphor absorption model for a wider range of conditions

Overall, this work presents a significant step forward in understanding, designing, and applying experimental techniques that use aerosol phosphor thermometry.

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