Technique Note

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Introduction to High-Speed UV/Vis Spectroscopy

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Introduction

We use light all the time to measure quantities you would not expect – we use light to measure kinematics (speed, acceleration), to measure stress and strain (digital image correlation), to measure fluid flow (particle image velocimetry, laser doppler velocimetry), and to measure temperature (pyrometry). In fact, all of this is done without even interacting with the system – we simply watch. Spectroscopy is a natural poetic extension of this process: if you can watch a system, you can determine what that system is made of all the way down to an atomic and molecular level.

Spectroscopy has a vibrant and colorful history in optics. Using the techniques developed throughout the 19th century, spectroscopy became the catalyst for which our understanding of the natural world blossomed into a rich tapestry of knowledge, each warp and weft woven with profound insights about the nature of light and matter from the unfathomably large to the invisibly small. From the large, one of the most astonishing revelations was that the composition of our Sun, a celestial entity once thought to be composed of an ethereal or divine substance, shares common elements with those found on Earth, specifically hydrogen and helium (helium of course with the prefix *heli-*, coined from the Greek *helios*, or Sun). To the small, the very electron, the most fundamental unit of charge, was confirmed in an experiment using the spectrum of sodium before even the idea of quantum mechanics entered anybody’s mind. Thus, spectroscopy established itself among the weird ways we can use light to measure unexpected quantities, and a rather important one at that.

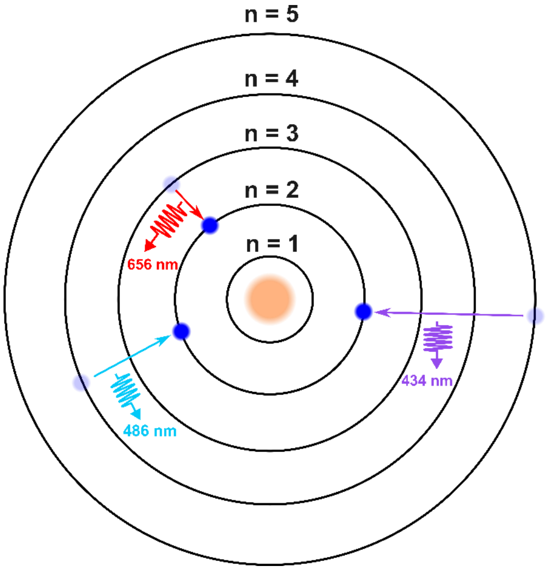

Figure 1 -- The hydrogen atom energy levels. Each quantum leap down to the n=2 energy level yields a photon of a specific wavelength.

How does it work?

Every atom or molecule has its own unique spectral signature based on its electronic structure, meaning that it can only absorb or emit a very specific combination of wavelengths of light. The canonical example to demonstrate this is the hydrogen atom, a single electron bound to a proton. In the hydrogen atom, the electron can only exist in certain discretized energy states, called its energy levels, shown in Figure 1 and labeled as *n*. This is remarkably unlike our everyday experience, since objects have a continuous availability of energy – after all, it’s not like you must throw a ball at 50 kph or 60 kph with nothing in between; you can always throw a ball harder or softer to impart more or less kinetic energy, respectively. Yet, on the atomic level, the electron must either absorb or emit these discretized energies in order to gain or lose energy with nothing allowable in between.

Specifically, the vector for energy transfer to and from the electron is the *photon*, or a small packet of light. The electron can absorb a photon to gain energy, or it can emit a photon to lose energy. As shown in Figure 1, the electron falls from its n=3 to n=2 energy state and releases a photon with the wavelength of 656 nm – red light.

Figure 2 -- Absorption spectrum of hydrogen. The electrons only take the wavelengths it needs to hop to higher energy levels.

Let's consider the case where we pass white light (a combination of all wavelengths) through hydrogen gas. The electrons will absorb a few specific wavelengths and leave the rest of the light untouched. What you would see in the visible range is shown in Figure 2 – the electrons have absorbed only the light which allowed it to traverse the energy levels. In this case, red light, cyan light, blue light, and purple light. This is one of the most famous spectroscopic series and is called the Balmer series, named after Johann Balmer, who derived an empirical formula to calculate the wavelengths of light which the electrons absorb. Such a spectrum is called an *absorption spectrum*.

Now let's consider the case where we pass a voltage through the gas, such as placing the gas inside of a gas tube and passing it through two electrodes. This will cause the electrons to absorb the electromagnetic energy and, after a certain amount of time, emit the energy back out as photons. This process is called *fluorescence* and what you will see is shown in Figure 3a. Note how it's the inverse of the absorption spectrum above and such a spectrum is called an *emission spectrum*.

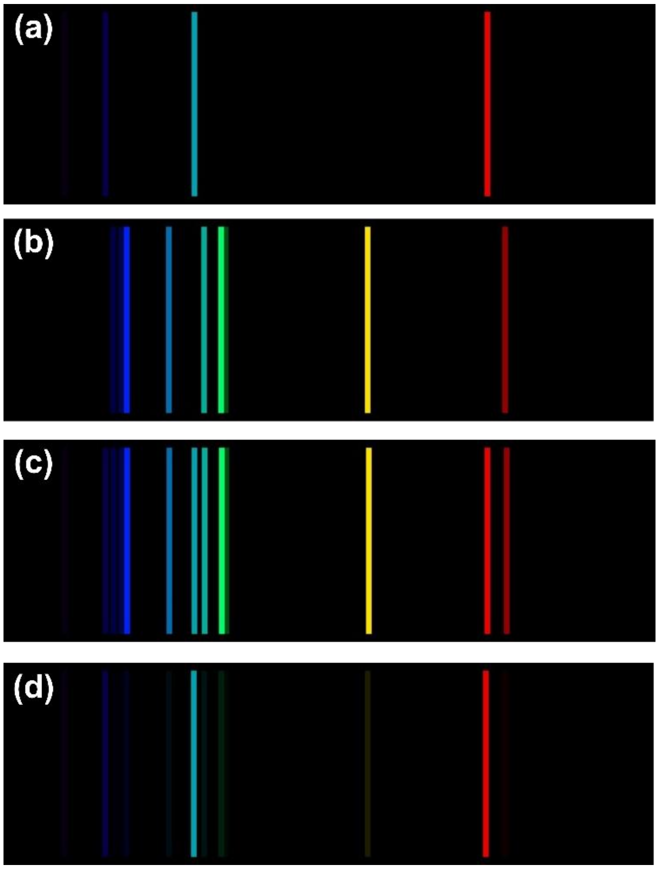

Figure 3 -- (a) Emission spectrum of hydrogen. (b) Emission spectrum of helium. (c) A gas with an equal mixture of hydrogen and helium. (d) A gas with an unequal mixture of hydrogen and helium, containing much more hydrogen.

The characteristic wavelengths are why each atomic or molecular spectrum is called a *signature*. It is truly unique to each constituent part of a system – only the hydrogen atom can emit the wavelengths above while something like helium, the next element on the periodic table, has a different spectral signature than hydrogen, shown in Figure 3b. The overall idea is that if you were to analyze the light from a system as shown in Figure 3c, you could say with certainty that your system is a combination of hydrogen and helium gas. To determine the specific proportion, you would look at the intensities of each line. In Figure 3d, the system consists of much more hydrogen than helium, as the hydrogen spectrum is much stronger than the helium spectrum.

How do we measure it?

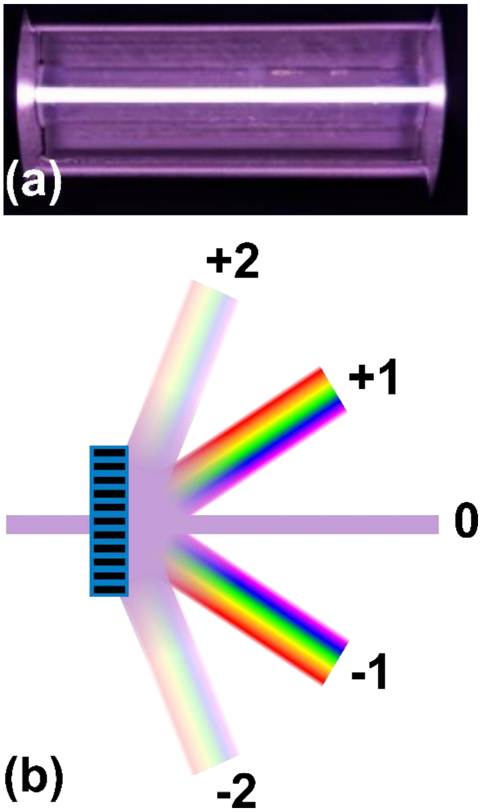

Figure 4 -- (a) A spectral tube of an unknown gas. (b) A diffraction grating separating out the fuchsia light into its constituent colors.

Actually, if you were to look at gas fluorescence, you would only see something like Figure 4a – a light fuchsia tinted light. Consider what happens when you combine red and green light: you observe yellow light. The same principle applies here as all of the spectral wavelengths combine to produce an *apparent* single color, so we seek a way to separate out the constituent wavelengths in order to produce a sharp spectral signature. What we need is called a *diffraction grating*, and its principle of operation is depicted in Figure 4b. Here, the light interacts with the many slits, grooves, blazes, or other sort of microscale periodic structure to emerge in different directions in a process called *diffraction* (hence, diffraction grating). The light's trajectory upon this normal incidence can then either be unaffected, deflected counter-clockwise, or deflected clockwise. The numbering to the right is called the *diffraction order* as there are many (discretized) angles the light can be deflected to either counter-clockwise or clockwise with respect to the zeroth diffraction order where the light remains unaffected. The crucial quality to understand here is that if the light is deflected into any diffraction order not zero, the specific angle within that order the light travels at is *wavelength dependent*. Thus, if the light is deflected into the +1 diffraction order, the light will disperse into its constituent elements with each wavelength taking a slightly different path. Depicted in Figure 4b is called a *transmission grating* but there are other types of diffraction gratings, such as a *reflection grating* which operates off the same principle except the light is reflected into its diffraction orders rather than transmitted and deflected. Most diffraction gratings you can purchase use what's called a *blazed surface* where its asymmetric grooved structure causes more of the light to be deflected into the +1 diffraction order for a brighter spectrum.

Figure 5a depicts the full visible spectroscopy setup:

1) The light passes through a lens to gather and focus as much light from the source as possible.
2) A slit aperture is placed at or near the focal length of the lens at (1). The purpose of the slit aperture is to improve the spatial resolution of your spectrum – by narrowing the slit, you are ensuring that the light is only coming from a single direction, preventing spectral broadening. However, the necessary drawback is that you lose light, much like the familiar apertures for a camera lens.
3) A second lens collimates (parallelizes) the light such that it will strike the diffraction grating as close to normal incidence as possible.
4) The diffraction grating, with its principles of operation described above in Figure 4.
5) A concave, parabolic mirror collimates (parallelizes) the light after the light has dispersed into its constituent wavelengths, allowing the light to strike the sensor normal for a sharp focus.

If everything is aligned properly and with enough light striking the sensor, what you should see would look something like Figure 5b, the UV-extended UV/Vis spectrum of diatomic nitrogen.

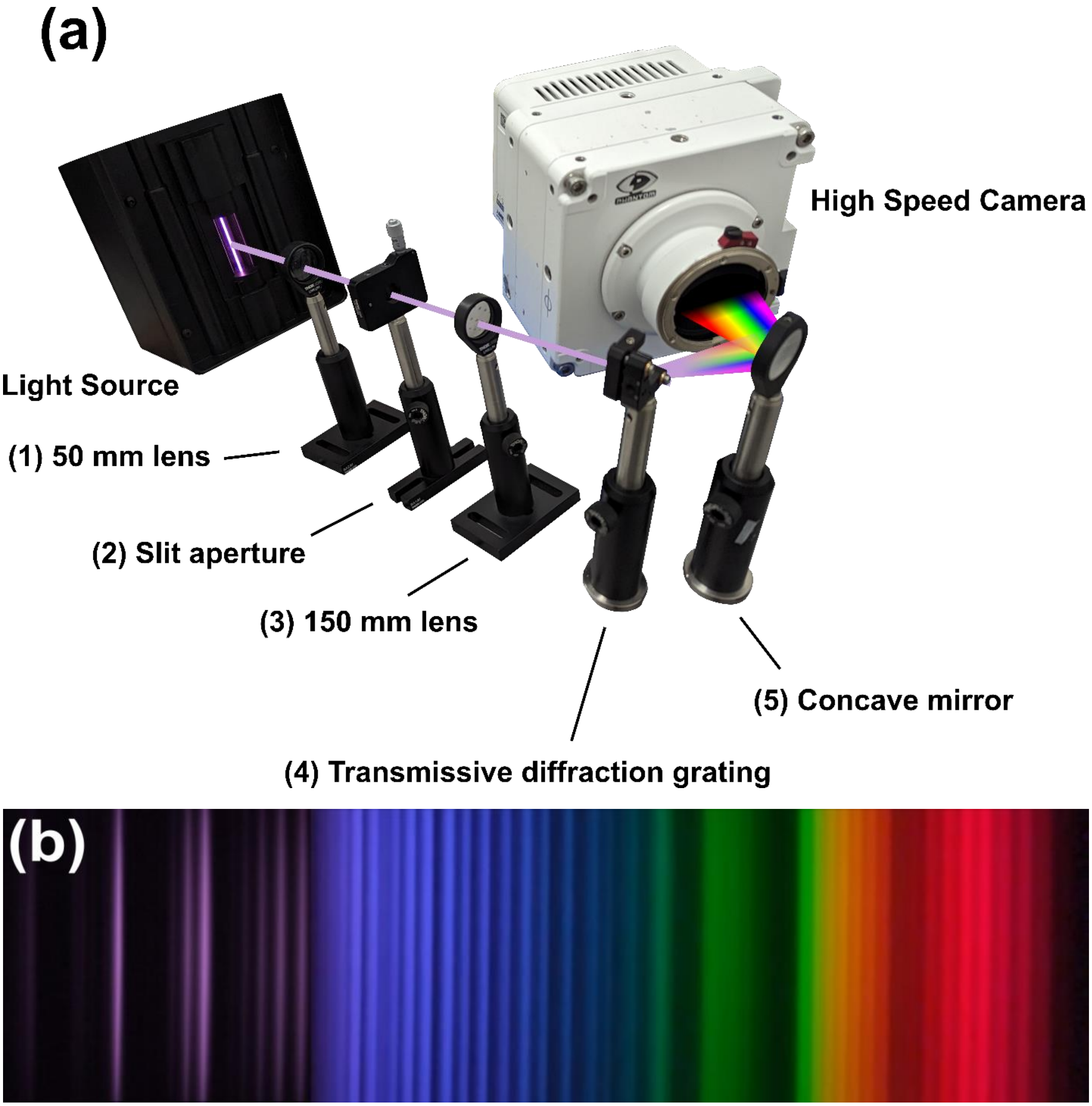

Figure 5 -- (a) Diagram of the full optical setup. (b) The resulting spectrum. This spectrum is stitched together between the UV and visible parts with the UV false-colored.

Wavelength Calibration

Let us consider the UV-A spectrum of diatomic nitrogen from 300-400 nm as shown by the false-colored fuschia lines towards the left of Figure 5b. These lines are called the *second positive system* and are of considerable scientific importance for several reasons:

- **Ubiquity**: Nitrogen is the most abundant gas in our atmosphere by a substantial margin, constituting approximately 78%. This abundance means that nitrogen emissions, especially those from the second positive system, are both: (a) more readily observable in a variety of natural and laboratory settings compared to emissions from less abundant molecules such as diatomic oxygen and carbon dioxide, and (b) commercially available and inexpensive to study.

- **Strong and Distinct Emission Lines**: The UV emissions from nitrogen are a lot sharper than the band-like spectrum of the visible regime. Such a feature makes the second positive system easier to detect and distinguish from noise or other spectral properties of other elements.
- **Chemical Stability**: Diatomic nitrogen is one of the strongest known electronic bonds, meaning it takes an extraordinary amount of energy to break apart diatomic nitrogen into its atomic form. Under similar conditions, diatomic oxygen and carbon dioxide will simply dissociate as reagents in a chemical reaction. Such a property makes diatomic nitrogen one of the primary indicators of energy transfer and distribution within a system, rather than indicative of chemical reactions.
- **Biologically inert**: Nitrogen is biologically inert, meaning it doesn't react well, if at all, with biological tissue. This is ideal for medical diagnostics whereas something like reactive oxygen, a highly flammable gas, should never be used.

Thus, we begin the procedure to map pixel position onto wavelength.

Index	Wavelength (nm)
A	315.93
B	337.13
C1	350.05
C2	353.67
C3	357.69
D1	367.19
D2	371.05
D3	375.54
D4	380.49

Table 1 -- Accepted values of the Second Positive System.

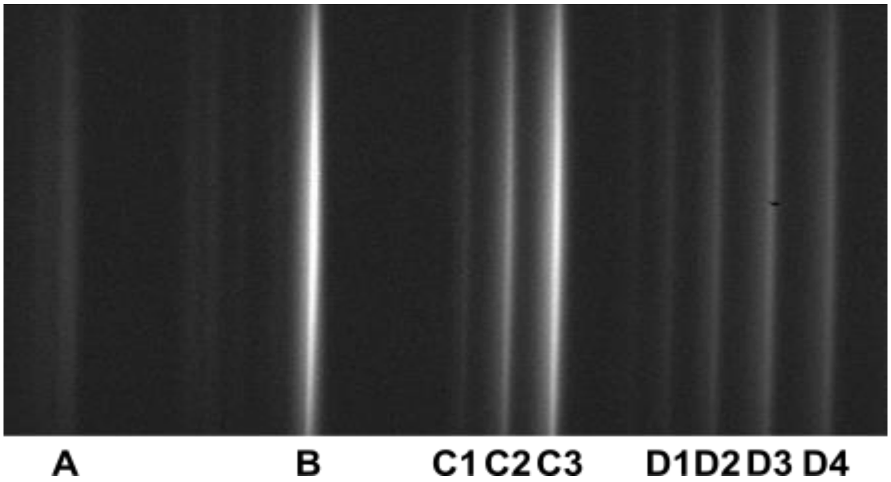

Figure 6 – Experimental data showing an image of the second positive system of Nitrogen taken with a UV-extended Phantom camera, wavelength range ~300-400 nm.

Upon inspection of the second positive system featured in Figure 6, we can see that there are four groups of lines, starting from the left: a singlet, another singlet, a triplet, and a quartet. Featured in Table 1 are the accepted wavelength values for these lines. We will assume that the mapping is linear such that each pixel position increment will correspond to the exact same increment in wavelength, i.e. 1 pixel pitch = 0.1 nm of wavelength, or perhaps 1 pixel pitch = 0.06 nm of wavelength, etc. With this assumption, we can choose any two values from Table 1 as guideposts and construct a linear function connecting the two points (and then extrapolate to the other wavelengths), but for this example we will choose indices A and D4 where no extrapolation is needed (since the line connecting indices A and D4 will already pass through every other point). A description of the linear function including the Python code and raw data used to generate the mapping can be found in Appendix A.

One final and extraordinarily important detail is that you don't just get one sample per wavelength per frame – each spectral line is just that: a *line*, with a spatial extension perpendicular to the wavelength axis. When this spatial extension is included in your analysis by a simple summation, your signal-to-noise ratio skyrockets since your signal data will far outpace the uncorrelated noise (technically speaking, the signal adds linearly while the noise adds in quadrature).

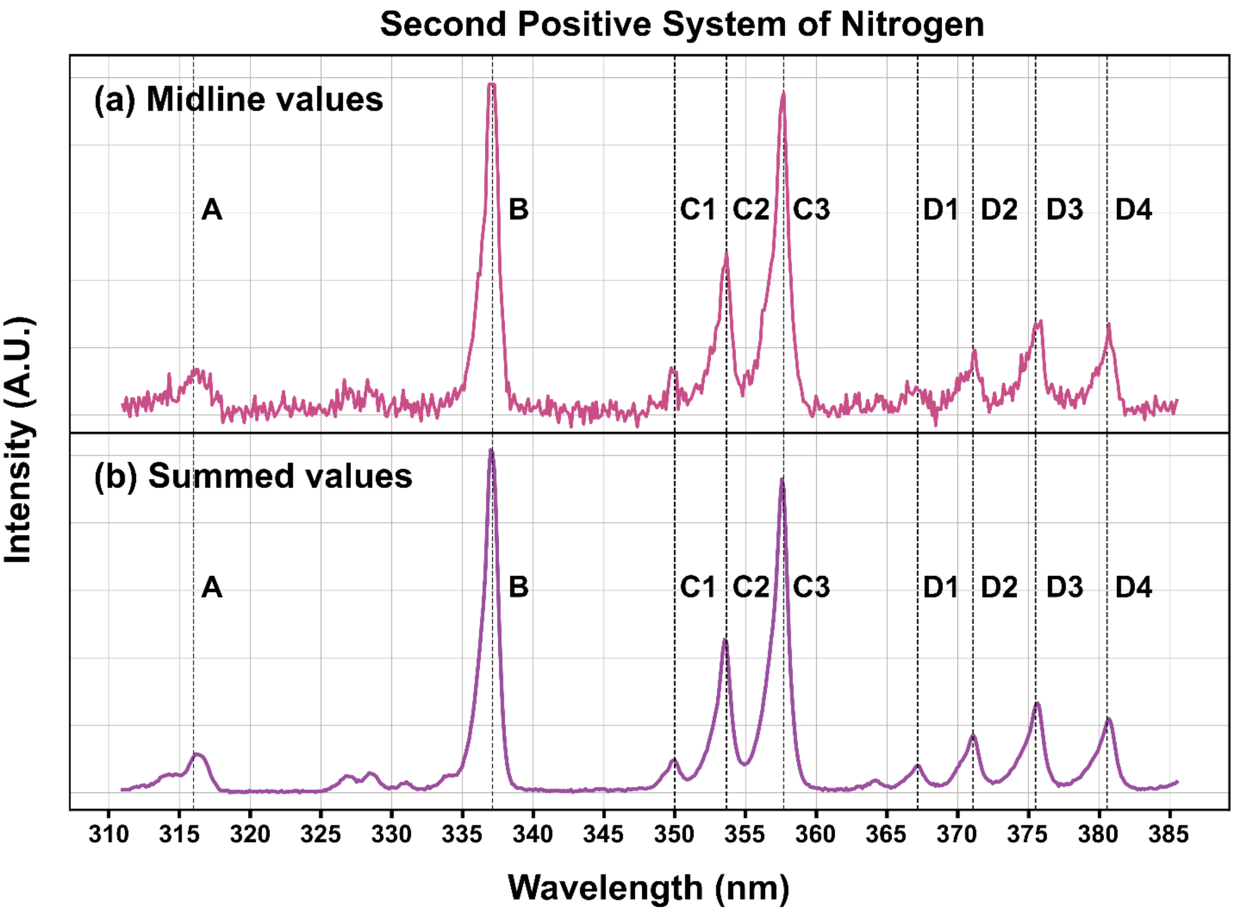

Figure 7 -- Results of mapping onto wavelength. (a) One data point per wavelength as plotted through the midline of each spectral line. (b) Summed up along the spatial extension of each spectral line. Notice that some features which would be indistinguishable from noise now lay manifest as actual signal, such as the small peaks between 325-335 nm, corresponding to real (but minor) transitions within the second positive system.

The full spectrum of the second positive system is now shown in Figure 7. Figure 7(a) includes a single row of data while Figure 7(b) sums up along the spatial extension of each spectral line. The mapping we use is 0.126 nm/pixel pitch but such a construction can change based on several factors, including the camera itself, size of the optics, spatial resolution desired, groove density of the grating, etc. The vertical dashed lines are plotted at the accepted values for the second positive system, demonstrating that our system is properly aligned and well-calibrated in wavelength for spectroscopic measurement. A quantitative analysis of our calculated values for the second positive system including error can be found in Appendix B.

Intensity Calibration

There are two terms which must be defined when talking about intensity: spectral **emittance** and spectral **irradiance**. Spectral emittance is the optical power per wavelength *emitted* by the source while spectral irradiance is the optical power per wavelength *received* at the sensor. For the following example calibration, we consider irradiance only – however, it should be noted that for absorption spectroscopy, you would typically use a light source to illuminate your system from the opposite side with an intensity that needs to be known *a priori* – after all, to know how much light was absorbed at each wavelength by your system, you would need to characterize the light source being absorbed. This can be done with a normal optical power meter.

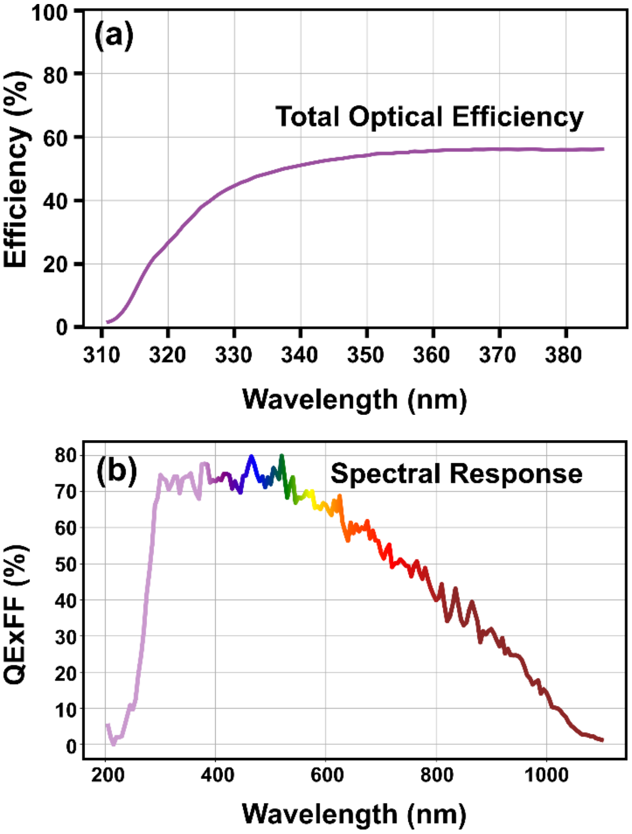

Figure 8 -- (a) Total optical efficiency within the UV-A range. (b) Complete spectral response of the UV-extended TMX 7510. The UV range (colored fuchsia) begins at about 400 nm. The visible range (rainbow colored) spans 400-750 nm. The IR range (dark red colored) begins at 750 nm.

While wavelength calibration is a straightforward procedure, it is considerably more difficult to calibrate for absolute irradiance. Any system contains three degrees of freedom which must be accounted for:

- **Transmission/reflection efficiency**: All optical elements are dispersive, meaning the response of the material changes based on the wavelength of light incident upon it. Windows in your home are transparent to visible light yet they are generally opaque to UV light, wherein the glass absorbs the UV light. Similarly, the door to your microwave oven can reflect microwaves while allowing visible light to transmit through.
- **Diffraction efficiency**: As shown in Figure 4b, diffraction gratings will transmute incident light into several diffraction orders. Only one of these diffraction orders will be useful for you and most common gratings will prioritize +1 order. Yet, any spectral energy outside of the order under consideration will be lost to your sensor.

Note that the total optical efficiency (meaning the fraction of light as a function of wavelength reaching the sensor after passing through all our optics) is shown in Figure 8a.

Spectral responsivity: The spectral responsivity of a CMOS sensor defines the efficiency of the pixels ability to convert photons into electrons (or charge). No CMOS sensor converts all light into electrons, as for a variety of reasons an incident photon might not be converted into a photoelectron that can be detected by the ADC circuitry. Additionally, this responsivity is dispersive, so such a responsivity depends on the wavelength of light incident upon the sensor. For the UV-extended TMX 7510, the spectral response curve is shown in Figure 8b.

The procedure for intensity calibration can be done with the following two steps:

1) **Convert pixel values into electrons and then into photons**: This can be done by using the system gain K from our EMVA 1288 spec sheet and the spectral response raw data from our own spec sheet. The system gain will provide the number of photoelectrons from the pixel values and then quantum efficiency will provide the total number of photons incident on the sensor over one

integration time (exposure). This is only true provided that no digital modifiers are applied to the pixel values (i.e., gain, gamma, etc.).

2) **Normalize for optical efficiency**: This can be done by dividing the total optical efficiency per wavelength of your optical elements by the number of photons per wavelength (irradiance) calculated in the first step. The purpose of this step is rescale the peaks based on true optical output from the source – for example, if you expect a very strong OH radical peak at 309.2 nm but your optics will only allow 5% of the light through at that wavelength, what you observe would be rather small compared to other spectral properties of other atomic interactions within the system. An important note is that **this normalization only produces valid data when your signal is appreciably greater than your noise**, i.e. high signal-to-noise ratio (SNR). When the signal is on the order of the noise, your rescaling will amplify the noise significantly as we see in Figure 9 towards the left-hand side when barely any light below 310 nm reaches the sensor.

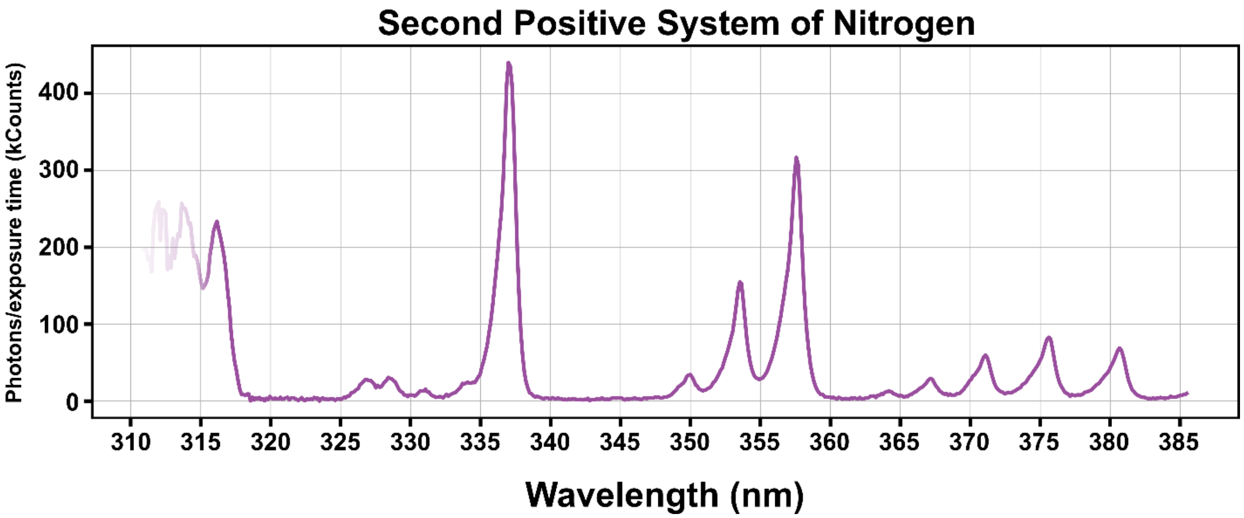

Figure 9 -- Rescaled spectrum of the second positive system of Nitrogen.

Figure 9 shows the resultant scaling of the y-axis. Note that since the optical efficiency is generally the same down to 350 nm (Figure 8), the spectral features remain in similar proportions for the C-triplet and D-quartet. Below 350 nm, the spectral features are rescaled to greater values, since fewer photons at those wavelengths reached the sensor. Note, specifically, that B is scaled to be greater than C3 now and A is scaled to be much larger than it was initially. Yet, once we move deeper into the UV, our SNR is too low as practically no light within this wavelength range reaches the sensor and our rescaling amplifies the noise significantly.

Intensity Calibration with Standard Candle

It is also possible to calibrate for intensity with a "standard candle" – a well-calibrated and well-characterized broadband light source such as a tungsten-halogen lamp. Pass this candle through all of your optical elements and incident upon the sensor and compare your spectrum to the spectrum of the standard candle – you can construct a function to map the received spectrum onto the expected spectrum for each wavelength. Then, for any future measurements, use the same function to rescale your spectrum as desired.

References

1. Lofthus, A., & Krupenie, P. H. (1977). **The spectrum of molecular nitrogen.** Journal of Physical and Chemical Reference Data, 6, 113-307. https://doi.org/10.1063/1.555546
2. Spec sheet for all UV-extended cameras can be found on our website here: https://www.phantomhighspeed.com/products/toolsandaccessories/uv-extended-cameras