INTRODUCTION:

UV/visible absorption spectrometry is a highly useful analytical technique with wide a range of applications. A major advantage is the high sensitivity compared, for example, to measurements using FTIR. On the other hand, most polyatomic molecules don’t have distinct “fingerprint” absorption bands in the UV/visible as they do in the IR, making specific identification of an individual compound in a complex mixture very difficult using UV/visible.

Some small polyatomics, e.g. NO₂, HCHO, SO₂, O₃, have some structure to their UV/visible absorption spectra and these can be used for specific identification and measurement. In fact, a technique known as “Differential Optical Absorption Spectrometry” (DOAS) based on UV/visible is used for measuring very small concentrations of species in ambient air. DOAS can detect very reactive species, including free radicals such as NO₃ and ClO, often down to part-per-trillion (ppt) levels.

One important aspect of the application of absorption spectrometry to quantitative measurements is the appropriate use of the Beer-Lambert Law (commonly known as “Beer’s Law”). This applies strictly only to a single wavelength. When more than one wavelength is present, and the different wavelengths have very different absorption coefficients, the usual Beer-Lambert Law breaks down, i.e. plots of absorbance vs. concentration become non-linear.

Equivalent to having more than one wavelength present is the use of low spectrometer resolution over a region where the absorption coefficient is changing rapidly. Under these circumstances,
the Beer-Lambert Law will not be linear, and will be a function of resolution. This experiment is
designed to demonstrate this for a molecule of atmospheric interest, NO₂. NO₂ photolyzes to
form ground state oxygen atoms, O(³P),

\[ \text{NO}_2 + h\nu \longrightarrow \text{NO} + \text{O(³P)} \]

which then reacts with O₂ to form O₃:

\[ \text{M} \]
\[ \text{O(³P)} + \text{O}_2 \longrightarrow \text{O}_3 \]

Due to its high toxicity, ozone is the air pollutant on which smog alerts are called. The Federal
Air Quality Standard for O₃ is 0.12 ppm = 120 ppb for one hour, not to be exceeded more than
once per year, i.e. if there is more than 120 molecules of O₃ per 10⁹ molecules of air, you have
exceeded the air quality standard and are damaging someone’s health!

In this experiment, you will measure NO₂ using UV/visible absorption used in the
conventional manner, as well as using the DOAS approach. You will see the effects of resolution
on the measured absorbances, as well as the effect of the equilibrium between NO₂ and its dimer,
N₂O₄:

\[ \text{N}_2\text{O}_4 \longleftrightarrow 2 \text{NO}_2 \]

\[ K_p = \frac{P^2(\text{NO}_2)}{P(\text{N}_2\text{O}_4)} = 0.163 \text{ atm (at 298 K)} \]

When you put NO₂ in these gas cells, it is really a mixture of NO₂ (which is brown...absorbs
light in the visible beyond 400 nm) and its dimer, N₂O₄, which does not absorb in this region.
The total pressure you measure is therefore the sum of NO₂ and N₂O₄, but it is only NO₂ which
you are measuring by absorbance:

\[ P_{\text{tot}} = P(\text{NO}_2) + P(\text{N}_2\text{O}_4) = P(\text{NO}_2) + \frac{P^2(\text{NO}_2)}{K_p} \]  \hspace{1cm} (I)

Here, \( P_{\text{tot}} \) is the measured total pressure in the cell. From eq. I, we can calculate the true pressure
of NO₂ in this equilibrium mixture:

\[ P(\text{NO}_2) = \frac{K_p}{2} \left( -1 + \sqrt{1 + \frac{4P_{\text{tot}}}{K_p}} \right) \] \hspace{1cm} (II)

**PROCEDURE:**

(Mnm is defined as the monochromator reading, not the actual wavelength)

**Part I. Calibration of the Monochromator Using a Mercury Arc Lamp**

*Treat all equipment with care and ease - do not force knobs to turn and do not move out of alignment!*

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1. **MAKE SURE THE POWER TO THE PHOTOMULTIPLIER TUBE IS OFF.** This is done by setting the C6271 (PMT gain) dial to zero.

2. Turn on the switch on the front of the monochromator. You will see some things flash on the Hand Scan device and then it will go blank. Press the button showing the black dot (●) and then press *Enter* to start the Hand Scan. You will see the following menu:

   Mono Drive *  
   0.000  *Edit

3. You need to let the Hand Scan know what the wavelength setting is on the monochromator (otherwise the two don't work together and you have no idea what wavelength is really exiting the monochromator). To do this, look at the wavelength setting on the counter at the back of the monochromator using the dental mirror so you can see the counter. It can be any value, depending on how it was last used.

   Press the *Cal* button, then press *Enter*, then *Cal* again. You should now see the following on the Hand Scan:

   Mono Drive  * Cal A
   0.000  *Edit

   Now use the number pad to enter the **actual reading** on the back of the monochromator, then press *Enter*.

   In order to set a wavelength, you will press the *Go To* button, put in the wavelength you want to go to and then press enter. The Hand Scan will set the monochromator to that wavelength. You can check that it is by watching the counter on the back.

4. Set monochromator to read 000 nm using the hand scan. This is the “0th” order and passes all light through the monochromator without dispersion. Do this using *Go To*.

4.5. Set the monochromator to 400 nm using the HandScan and re-calibrate with the actual wavelength shown on the back of the monochromator. Do this in the same way as above.

5. Open the main valve to the nitrogen tank and the last valve of the tank to purge the mercury arc lamp (otherwise excess amounts of ozone will be formed). You should wait approximately 5 minutes to allow complete nitrogen purging before turning on the lamp. Ask your TA for help if you cannot get the tank open or if you never handled pressurized gas cylinders.

6. There are two exits from the monochromator. One has a micrometer handle for setting the exit slit width and has a photomultiplier housing attached to the exit. The other exit is a hole covered by a frosted glass plate or “screen” with a fixed slit width and a shutter which you can
use to visually observe what would normally be passing through the slit onto the photomultiplier tube (PMT). As you look at it from the top, turning the knob clockwise directs the beam into the photomultiplier, counterclockwise to the frosted glass plate. There are only two positions for this knob, it should not turn all the way around. TURN THE KNOB GENTLY!

7. After the 5 minutes of purging has passed, turn on the mercury lamp. Leave the nitrogen flow on all the time while using the Hg lamp. Set the mercury lamp and its housing so that the light is focussed through the two optical lenses onto the entrance slit of the monochromator. Do NOT look directly at the mercury lamp source. Set the entrance slit width to around 300 µm. To set the slit widths, the micrometer is turned clockwise from zero, and each small division is 100 µm. Therefore, 50 µm is estimated as half way between the zero and 100 µm marks. If you are unsure, check with your TA how to operate the micrometers.

8. Open the cover over the frosted glass plate so that you can see the whole plate. Gently turn the knob on top of the monochromator to the position where you see the blue-violet light on the frosted glass. Be careful not to move the monochromator while opening the cover of the frosted glass plate. Ask your TA for help if the cover seems to be sticking.

9. Use the Hand Scan device to set the wavelength to 400 nm. Scan slowly forward to the monochromator reading of 700 nm. To set parameters, press the Scan Menu button, then Enter. It now asks you for the "Start" wavelength. Put the number in, then press Enter. It then asks you for the "end" wavelength. Put it in and press Enter. Proceed through the rest of the selections in a similar manner. A reasonable value for the scan rate for this part is 5 nm/sec. The menu showing "Trigger" should be at the "off" setting. Set the entrance slit width to 200 or 300 µm. Press Run to begin scan.

10. During this scan, watch the colors as they appear in the slit on the frosted glass plate. You will scan by several emission wavelengths that will reveal the color of the wavelength that the mercury lamp is emitting. When you detect (by the color appearing on the glass) the mercury emission lines, write down the approximate monochromator wavelength reading when the line is in the middle and the color that was detected. A low pressure mercury-vapor lamp produces intense lines at 404.7, 435.8 (blue), 546.1 (green), 577.0 and 579.1 (yellow doublet) and 691 nm. The monochromator is not accurately calibrated in all wavelength regions and therefore you may see the emission colors at different monochromator readings than the above. This is why you are doing this - to calibrate the wavelength setting of the monochromator.

If you want to see the lines in a stationary fashion, use the GoTo button to go to one of the above wavelengths and you should see the corresponding color in approximately the center of the frosted glass plate.

11. Set the entrance slit to 150 µm and the exit slit width to 50 µm.

12. Close the frosted plate. Turn the knob on the top of the monochromator to the other position where the light is now directed to the variable exit slit and photomultiplier. Be careful not to move the monochromator when doing this; otherwise you will have to start over…
Note: It is important that the frosted plate is always closed when the photomultiplier is exposed to the light in the monochromator. A photomultiplier tube which is on (i.e. has the gain turned up) may be seriously damaged by large amounts of light.

13. Turn the power on to the photomultiplier by turning the gain dial to 45. This is done by turning the dial 4 full turns. Open the black shutter (on the PMT) by pushing the shutter in (away from you) to the open position.

14. Open the program “LoggerPro 3.2” located on the desktop of the computer. Make sure that the program that opens is a voltage vs. time plot. Press the “Data Collection” button located in the toolbar (looks like a stopwatch on an x-y axis drawing) and set up the collection parameters. Calculate how long your scan should take and enter this value in seconds into the box labeled “collection length”.

\[
\text{scanning time} = \frac{\text{scan range (nm)}}{\text{scan speed (nm/s)}} \times 1.1
\]

Use 5 scans per second for all scans in the LoggerPro 3.2. You will need to do this calculation each time you change scan parameters on the HandScan. Factor of 1.1 makes sure that the acquisition program does not stop before the monochromator does.

15. Take a spectrum by scanning the monochromator at a maximum scan rate of 0.5 nm per second over the 400 to 700 nm range (scan range = 300 nm). Press “Collect” on the LoggerPro program and at the same time you press run on the HandScan, so that you know where 400 nm begins on your spectrum. You will have to move the grating back to 400 nm before starting the scan by using Go To. You can figure out the conversion between wavelength and time by using the scan speed and the start wavelength from the HandScan. This will make the data collection stop at the same time as the monochromator’s scan. Copy and paste the data from the scan into an Excel spreadsheet, making sure to write down the name under which each scan is saved.

Note: Never scan the monochromator past 1000 nm. If this happens, the wavelengths on the monochromator will need to be re-calibrated as in Part I.

16. Make sure that these parameters are written with the name of the Excel file to which they correspond to avoid confusion later. Remember to press stop on the LoggerPro immediately when scan is complete. As usual, write down all parameters of spectra including starting and ending wavelengths, scan rate, LoggerPro parameters, PMT gain, and entrance and exit slit widths.

17. When the scanning has completed, turn off the mercury lamp and close all valves to the nitrogen tank. Temporarily close the shutter on the photomultiplier tube and turn the gain back to zero. You will be using the white light source for the rest of this experiment.

Part II. Spectrum of the White Light Source
1. Double check that the entrance slit is set at 150 µm and the exit width at 50 µm. Carefully place the white light source in the same holder that the mercury arc was in. Since the white light source has its own collimating lens, remove the collimating lens closest to the white light source. Turn on the white light source by plugging it into the power strip and check the path (should only go through the one additional lens and then into the monochromator). Make sure the white light is being focused on the slit. Adjust the orientation of the source if it is not.

2. Open the cover over the frosted glass plate again. Turn the knob on top of the monochromator so that the light strikes the frosted plate.

3. Scan forward from 400 to 700 nm. During the scan, watch the colors as they appear on the frosted glass plate. Compare what you see to what you saw when you scanned the mercury light.

4. Close the frosted plate cover, and turn the knob on top of the monochromator back to the PMT position. Do not turn the PMT on while the frosted plate cover is open.

5. The PMT power supply should already be on. Turn the gain on the PMT up to 31 (3+ whole turns). Remember to set the data collection parameters in LoggerPro so that they match up with the new scan settings.

6. Scan forward and record the spectrum from 400 nm to 700 nm at a rate of 1 nm/sec.

Part III. Resolution Studies

1. Now record a spectrum of the white light source from only 400 nm to 500 nm at the same scan rate you used for part II, but with the exit slit width at 1000 microns. Entrance slit width should be set at 150 µm. Check that the PMT power supply is turned on and set it to the maximum sensitivity without cutting off any of the spectrum (i.e., the output voltage should be in the range that LoggerPro can comfortably digitize). Be sure to first get a zero reading by placing an index card in the path of the light and allow the computer to record this zero level for a few seconds before and after acquiring a spectrum. You need an accurate zero point reading in order to complete the calculations.

2. Between the optical lens and the white light source, place the ~23 Torr NO2 cell with the clamp provided.

3. Keeping the same sensitivity of the computer as well as other monochromator settings from #1 (part III), take a spectrum of the NO2 cell in the same wavelength region. Be sure again to include the zero point readings.

4. Repeat these scans (with and without NO2 cell) for exit slit widths of 500, 100 and 50 microns. Entrance slit width should stay at 150 µm during all of these scans. Be sure to record the zero points! Note that the sensitivity (i.e. PMT gain and PC sensitivity voltage) must be kept
the same for each white light source and NO₂ cell that are scanned at the same slit width. Otherwise, it is difficult or impossible to compare $I$ to $I₀$.

**Part IV. Beer-Lambert Law as a Function of Resolution and 2 NO₂ ↔ N₂O₄ Equilibrium**

Repeat Part III for the NO₂ cells of ~3 Torr, 7 Torr, and 43 Torr at exit slit widths of 50, 100, and 500 microns (keep entrance slit width at 150 microns). Remember to include zero point readings before and after each spectrum. Also, record the total pressure inside the cell (~760 Torr).

Once again, it is essential that you have a white light source spectrum for the exact combination of exit slit width, PMT gain, and voltage sensitivity on the digitizer for each of the NO₂ spectra. If you do not have this, it is difficult or impossible to compare $I$ to $I₀$.

**Part V. Determination of Pressure of NO₂ in the “Unknown” Cell**

Repeat Part III for the “unknown” cell, only use the exit slit width of 50 microns.

**Shutdown.**

Ask your TA for assistance with the shutdown procedure. Turn the gain on the photomultiplier down to zero, close the PMT shutter, and make sure the frosted plate is covered. Unplug the white light source and make sure the mercury lamp power supply is off. Check the nitrogen tank to make sure it is closed (close the valves on the tank and regulator). Turn off the monochromator at the bottom front. Close the program (make sure all your data files are saved). Finally, please clean-up the area as well as possible for the next group.

**CALCULATIONS:**

**Part I.**

Compare the recorded spectrum with your observations. Assign the monochromator wavelength reading to your recorded spectrum. Graph the monochromator wavelength reading (y axis) as a function of the actual wavelength (x axis, given above), derive a least square fit to the points and then use this equation to calculate all wavelengths and their corresponding monochromator nm (Mnm) using a spreadsheet program. Show all work. You have completed the monochromator calibration.

**Part II.**

There are no calculations for this part; however, do comment on the general shape of the light source spectrum and compare it to the low pressure mercury lamp spectrum. Be sure the
spectrum Mnm wavelengths have been converted to actual wavelengths (using your calibration data).

Part III.

Calculate both the conventional absorbance, defined as \( D = \log_{10} \left( \frac{I_o}{I} \right) \), and the differential absorbance, defined as \( D' = \log_{10} \left( \frac{I_o'}{I} \right) \) where \( I_o \) is the intensity of the source at that wavelength (which you have measured separately) and \( I_o' \) is the intensity without the peak absorption as shown in the attached figure. Do this for 448 nm absorption band. Note: To find the 448 nm band on your recorded spectrum, the calibration curve will be needed.

Plot both \( D \) and \( D' \) as a function of exit slit width at 448 nm. From this plot, what exit slit width appears to be the best to use for such studies? Why?

Hint: Also discuss differences between the different exit slit widths, e.g., the difference between the 1000 \( \mu \text{m} \) and 50 \( \mu \text{m} \) exits in terms of peak shape.

Part IV.

Measure and calculate \( D \) and \( D' \) for all spectra at 448 nm. Plot both \( D \) and \( D' \) as a function of the total pressure for each exit slit width. (The total pressure is that marked on the cells themselves.) Derive a least squares fit to the linear portion of the data points. Are your plots linear? If not, why not?

Now calculate the true equilibrium pressure of NO\(_2\) using the equations provided above and plot both \( D \) and \( D' \) as a function of \( P_{\text{NO}_2} \). What difference does this make to the linearity of the plots compared to those as a function of \( P_{\text{tot}} \)?

Part V.

Plot two calibration curves using both \( D \) and \( D' \) at the 50 micron exit slit width as a function of NO\(_2\) pressure. Derive a least squares fit to the linear portion of the data points. Using your measured values of \( D \) and \( D' \) of the “unknown”, what is the NO\(_2\) pressure in this cell? Calculate standard deviations and confidence limits.

What to include in your write-up:
- follow guidelines given in “Notice to Authors” from the Journal of Physical Chemistry: and the class handout
- in addition make sure to include the following:

Abstract
- Concise and short explanation of what was done and state your results with errors.

Introduction
- State the scientific motivation for this research.
- What are the scientific objectives?
- Explain Beer’s Law and derive pertinent equations relating to this experiment.

**Experimental**

**Part I:**
- Describe in detail all the major components of this experimental set-up.
- Include a hand-drawn (or better yet - a computer generated) detailed diagram of the experimental set up. Include a separate detailed diagram of the monochromator.
- Explain how data will be analyzed, i.e., equations?

**Part II:**
- Describe what you saw on the frosted glass plate for the white light source and compare to what you saw with the mercury light. Comment on the differences and the reasons for this.

**Part III:**
- Draw and describe the NO2 cells, what type of material are they made out of?
- What is the source of the chemicals used?

**Results:**
- Show all of your work! Using a computer program for linear regressions is acceptable, but be sure to include the actual least squares fit line as well as the resulting equation. Work out in long-hand the error in the calibration curve for the NO2 data.
- Remember that this lab report should look like it is ready to submit for publication - be organized!

**Discussion**
- Answer and discuss all previously asked questions included in this lab text .
- Comment and discuss results and possible errors from each section (Part I through Part V).
- Discuss data and graphs and especially the issue of linearity versus non-linearity and effects of resolution and equilibria (relate this to your introduction to Beer’s Law).