UV/VIS spectroscopy of d and f-electrons

This laboratory requires a laboratory report.

Introduction

The fourteen $4f^n$ orbitals are filled across the lanthanide series of elements (La-Lu), much like the ten $3d^n$ orbitals are gradually filled in the first transition metal series (Sc-Cu). Many of the lanthanides readily form divalent or trivalent ions in solution. Other oxidation numbers are possible too, but are less common. The lanthanides in particular have a strong preference for Ln^{3+}. Both series tend to produce colored salts because the partially filled shells facilitate electronic transitions in the visible. In a flame where we have isolated ions in a hot plasma these transitions lead to sharp absorption peaks that can be used to determine small amounts of the element by Atomic Absorption Spectroscopy. In solution or solid state this is different because the environment plays a role and *spectral broadening* is the result.

Broad absorption bands for d-d transitions

The transition metals have very broad d-d absorption bands that very little to do with the atomic spectrum and can only be understood in terms of *molecular* orbitals. The most important mechanism that causes such transitions to be broad is a strong coupling of electronic transition to the vibrationally excited states of the molecule (vibronic coupling).

Sharp bands for f-f transitions

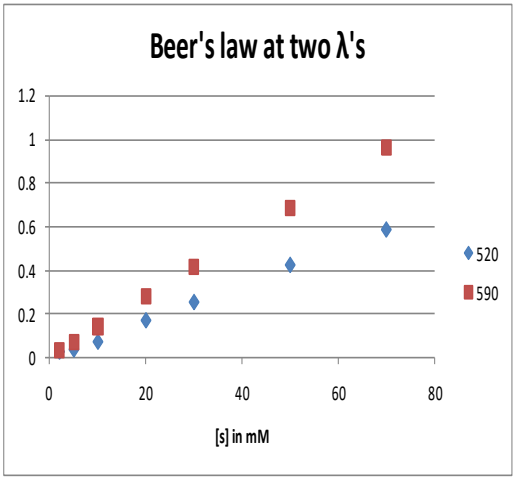
Lanthanide ions in solution have absorption spectra that strongly resemble the isolated atomic spectra, but the overlap with the environment is not negligible. Transitions between f-levels (*f-f* transitions) are relatively weak because the strongest mechanism (electron dipole coupling) is parity forbidden. Only magnetic dipole transitions are observed and they are generally much weaker. However through interaction with the environment (ligands) the parity rule can be broken a bit and this will enhance the absorption. So even f-elements are not entirely insensitive to the environment in solution

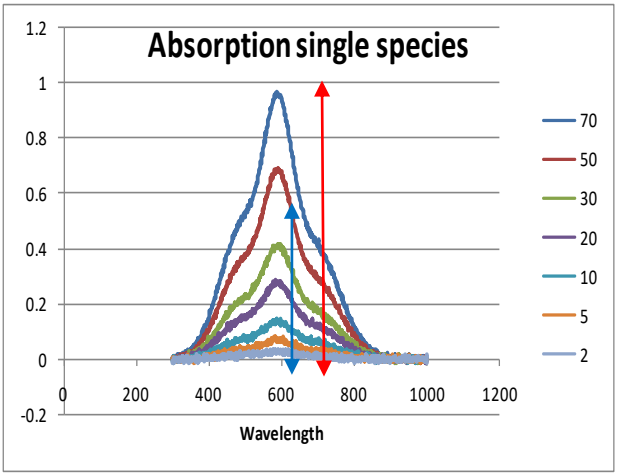
Lambert-Beer in mixtures

In a solution of a single component that absorbs over a range of wavelengths we can apply Beer's law at *any* wavelength that is absorbed by the solute s:

$A_\lambda = \varepsilon_\lambda.[s]$

It is usual to take the *maximum* of a peak in the spectrum as your working wavelength, because the *sensitivity* $S = dA/d[s] = \varepsilon_\lambda$ is maximal there. However, this is not necessary; we could take a different part of the spectrum. It just has a different value of ε_λ!





If the peak of the absorption exceeds A = 1.0 - 1.5, the measurement loses linearity. Remember that 90% of the light is absorbed if A = 1.0 so only 10% of incident light makes it to the detector. In such cases, it is actually better to use the side of the mountain, not the peak.

If you have two species, say s and t, in solution and the spectra overlap the measured absorbance at one wavelength is always a combination of two effects:

$$A_\lambda(\text{total}) = A_\lambda(s) + A_\lambda(t) = \varepsilon_\lambda(s).[s] + \varepsilon_\lambda(t).[t]$$

Unless the peaks happen to be exactly at the same wavelength the peak of one would be a hill side of the other and vice versa. It is often *not* possible to pick a wavelength where only one species absorbs (especially for d-ions!). Nevertheless we can still measure both concentrations [s] and [t] if we measure at (at least) *two wavelengths*, e.g. the peak of one and the peak of the other:

$$A_{\lambda 1=S\text{-peak}}(\text{total}) = A_{\lambda 1}(s) + A_{\lambda 1}(t) = \varepsilon_{\lambda 1}(s).[s] + \varepsilon_{\lambda 1}(t).[t]$$
$$A_{\lambda 2=T\text{-peak}}(\text{total}) = A_{\lambda 2}(s) + A_{\lambda 2}(t) = \varepsilon_{\lambda 2}(s).[s] + \varepsilon_{\lambda 2}(t).[t]$$

We can write these equations as a matrix product

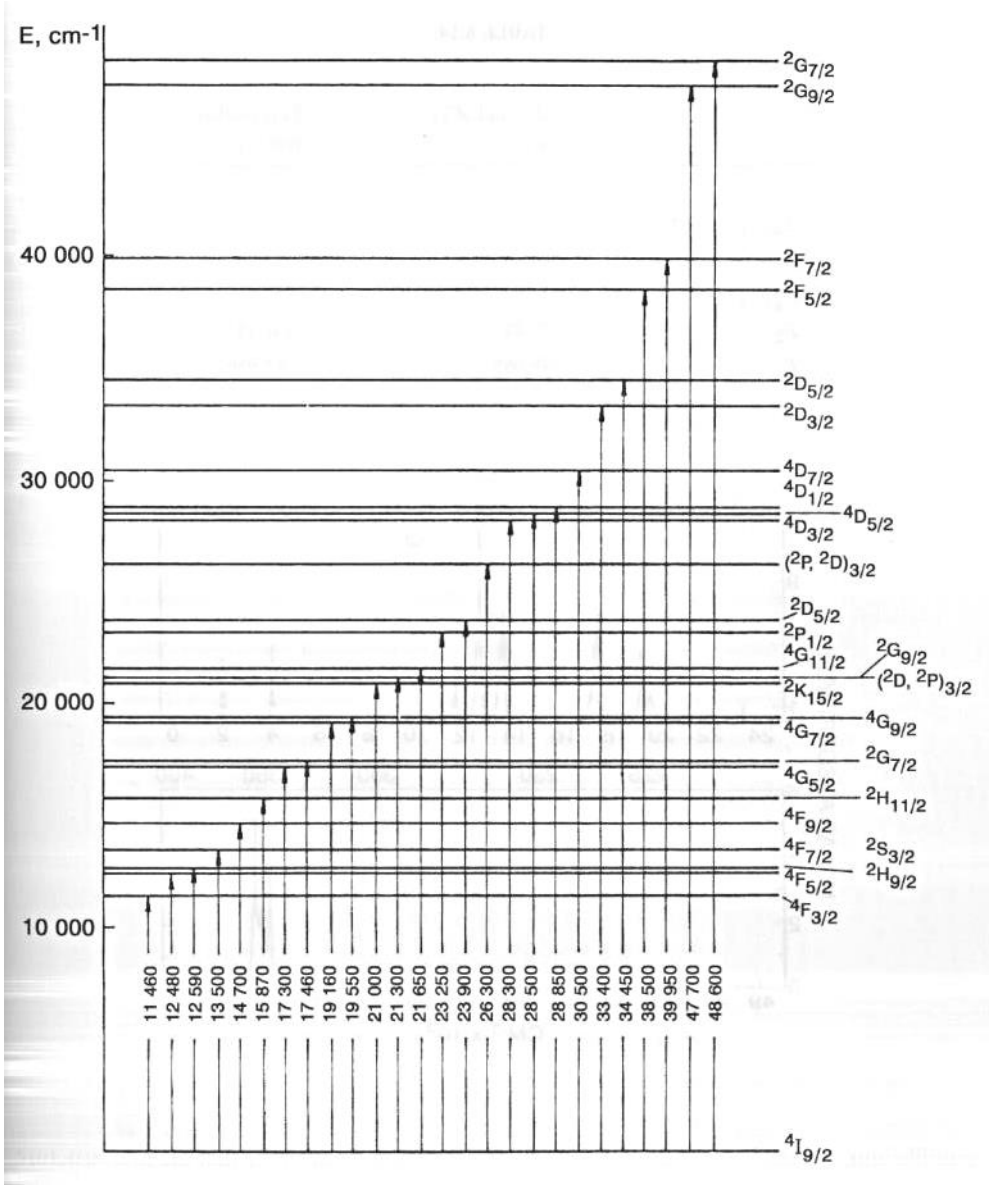
$$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} \varepsilon_1(s) & \varepsilon_1(t) \\ \varepsilon_2(s) & \varepsilon_2(t) \end{pmatrix} . \begin{pmatrix} [s] \\ [t] \end{pmatrix}$$

Provided we calibrate the four extinction coefficients $\varepsilon_\lambda(x)$ we can solve for the concentrations [s] and [t]:

$$\begin{pmatrix} [s] \\ [t] \end{pmatrix} = \begin{pmatrix} \varepsilon_1(s) & \varepsilon_1(t) \\ \varepsilon_2(s) & \varepsilon_2(t) \end{pmatrix}^{-1} . \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$$

We could use more wavelengths (of which we have a spectrum full!) but then the matrix **ε** with extinction coefficients will not be a square, so we should use a generalized inverse like $(\boldsymbol{\varepsilon}^T\boldsymbol{\varepsilon})^{-1}\boldsymbol{\varepsilon}^T\mathbf{A}$ rather than a simple $\boldsymbol{\varepsilon}^{-1}\mathbf{A}$. This would turn the calculation into a regression job.

These are the calculated energy levels for the f^3 ion Nd^{3+} and its f->f transitions. The energies are given in cm^{-1} (i.e. wavenumbers, note that wavelength[nm] = 10,000,000*wavenumber[cm^{-1}]). The transition to the state way in the UV cannot be observed because at those energies there are also other (much stronger f->d) transitions.



Lab instructions

The TA will provide you with stock solutions of a 0.2 M Nd^{3+} (aqueous nitrate) and a 0.2 Cu^{2+} (aqueous nitrate). These values assume you are using a 1.0 cm path length cuvette. A mixture of neodymium and copper nitrate of unknown concentrations will also be provided:

- From the two metal solutions prepare four dilutions: 1:1, 1:2, 1:5 and 1:10.
- Collect spectra from 400 to 800 nm. For the analysis we will use the absorbances at 521, 573, 640 and 680nm.

- Record the absorption spectra of the stock solutions and the four dilutions and write down the five absorbance values for each of the four wavelengths. Pay attention to the baseline. Plot the spectra in Excel or Igor and examine a portion of the spectrum that has little absorption (i.e. is relatively flat). If it differs from zero by more than 0.005 you should add (or subtract) a constant to the entire spectrum. Since absorbances may be small in this experiment, small offsets may affect the result. This procedure will eliminate such artifacts.
- Record the spectrum of the unknown and write down the absorbance at the same 4 values. Save this spectrum as well. You may want to compare the spectra later in your analysis.
- Export the data and save the files. Use suggestive shorthand nomenclature such as Nd02.dat, Nd01.dat, Nd005.dat for the 0.2 M, 0.1 M and 0.005 M solutions, respectively.

Data work up

Combine your absorbance values from multiple runs to determine the molar extinction coefficients of both ions at 521, 573, 640 and 680 nm by linear regression.

Prepare a table with the values of the extinction coefficients for the two species at the four wavelengths in column 1 and 2 and the absorbance of the unknown at those wavelengths in the third column. Then perform a regression of column 3 against 1 and 2. Report the concentrations of both species in proper 2/15 format.

Open the exported spectral files in Excel or Igor. Examine the spectra of the dilutions in the spectral region between 450 and 750 nm. Identify which transitions are responsible for the neodymium spectrum. These limits are chosen to include the 4 wavelengths and to frame the data nicely for making figures.

Determine the concentration of unknowns using the matrix method. For our purposes we will use a 2x2 matrix. Choose two of the wavelengths that are appropriate. Appropriate wavelengths should have relatively high absorbance for one species and low for the other, one for Nd^{3+} and one for Cu^{2+}. Use Excel to find the matrix inverse and solve the matrix equation. For a 2x2 you can always check your answer by hand, solving two equations with two unknowns. The brute force method does not work for a 3x3 or larger matrix, which is why the matrix method is so powerful. Here we are using the simplest case to learn the method.

Report the values of the extinction coefficients with 95% CI and the concentrations of the two species in the unknown mixture. Also report the errors in those concentration using appropriate propagation of error.