

	O	P
46	0.05328	(Co ²⁺)
47	0.1125	(Ni ²⁺)
48	0.1022	(Cu ²⁺)

Figure 19-9. The solution matrix .

DECONVOLUTION OF SPECTRA

The resolution of a complex absorption spectrum into individual absorption bands may be necessary if information about the position, height or width of individual bands is required. There are a number of computer programs designed for the deconvolution of spectra, but you can do a reasonable job with Excel.

The procedures described below were developed for the deconvolution of electronic absorption spectra (UV-visible spectra) but are equally applicable to the deconvolution of infrared, Raman or NMR spectra. UV-visible spectra differ from vibrational spectra in that the number of bands is much smaller and the bandwidths are much wider. Band shape may also be different. UV-visible spectra are also usually recorded under conditions of high resolution and high signal-to-noise. Spectra from older instruments usually require manual digitization from a spectrum on chart paper, at e.g., 10 nm intervals. With the widespread use of computer-controlled instruments, it is a simple matter to obtain a file of spectral data at, e.g., 1 nm intervals. In fact, it may be necessary to reduce the size of the data set in order to speed up calculations.

MATHEMATICAL FUNCTIONS FOR SPECTRAL BANDS*

A symmetrical spectral band is described by three parameters: position (wavelength or frequency corresponding to the absorption maximum), intensity (absorbance or molar absorptivity at the band maximum) and width (usually the bandwidth at half-height). The band shape functions most commonly used for deconvolution are the Gaussian function and the Lorentzian function. Both are symmetrical functions. UV-visible spectra generally have a Gaussian band shape. The Lorentzian function is useful for the simulation of NMR spectra. The log-normal band function has been applied to unsymmetrical spectral band shapes.

Many spectral bands can be closely approximated by a Gaussian line shape when the independent variable ν is in energy units, e.g., cm^{-1} . The absorbance A at a wavenumber ν is given by equation 19-1, where A_{max} is the band maximum, ν_{max} is the wavenumber of the band maximum and $\Delta\nu$ is the half-width.

$$A = A_{\text{max}} \exp \left[- (4 \ln 2) \frac{(\nu - \nu_{\text{max}})^2}{\Delta\nu^2} \right] \quad (19-1)$$

* P. Pelikán, M. Čepčan and M. Liška, *Applications of Numerical Methods in Molecular Spectroscopy*, CRC Press, Boca Raton FL, 1993.

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The corresponding equation for a Lorentzian line shape is given by equation 19-2.

$$A = \frac{A_{\max}}{1 + 4 \frac{(v - v_{\max})^2}{\Delta v^2}} \quad (19-2)$$

For unsymmetrical bands, the equation for the lognormal line-shape is

$$A = A_{\max} \exp \left\{ -\frac{\ln 2}{(\ln \rho)^2} \left[\ln \left(\frac{(v - v_{\max})^2}{\Delta x^2} \frac{\rho^2 - 1}{\rho} + 1 \right) \right]^2 \right\} \quad (19-3)$$

for the region $v \geq v_{\max} - (\Delta x \rho / (\rho^2 - 1))$ and $A = 0$ elsewhere. The asymmetry parameter ρ is given by:

$$\rho = \frac{v_R - v_{\max}}{v_{\max} - v_L} \quad (19-4)$$

A simpler form of the Gaussian band shape, where σ is simply treated as an adjustable parameter, is given in equation 19-5. This is the equation that will be used in the following treatment. By using an embedded chart to compare calculated and experimental data, you can fairly easily find a set of A_{\max} , v_{\max} and σ values that approximate the band shape, to use as initial guesses for the deconvolution procedure outlined in the box on the following page.

$$A = A_{\max} \exp \left[-\frac{(v - v_{\max})^2}{\sigma^2} \right] \quad (19-5)$$

DECONVOLUTION OF A SPECTRUM: AN EXAMPLE

The spreadsheet shown in Figure 19-10 illustrates the deconvolution of the UV-visible spectrum of a mixed-ligand complex of nickel(II). Four bands are apparent in the spectrum, one a weak shoulder lying between relatively intense bands at approximately 350 and 550 nm. The fourth band appears only as the tail of a fairly intense band lying at longer wavelengths.

The formulas in cells C10 (converting wavelength to wavenumber) and D10 (calculating the Gaussian band profile of band 1) are:

$$\begin{aligned} &=10000/A10 \\ &=band1 A_0 * EXP(-(((C10-band1 max)/band1 s)^2)/2) \end{aligned}$$

The Solver was used to vary the values in cells D4:F6 and G4:G5 to make cell I7 a minimum. Because the data did not permit a complete resolution of band 4, cell G6, the bandwidth parameter for band 4, was held constant at the reasonable value of 1.5. The results are shown on the spreadsheet. The resolved spectrum (solid line), with the four bands (broken lines), is shown in Figure 19-11.

The λ_{\max} values for bands 2 and 4, from other experimental measurements, are 445 and 880 nm, respectively.

(19-1)

Deconvolution of a Spectrum

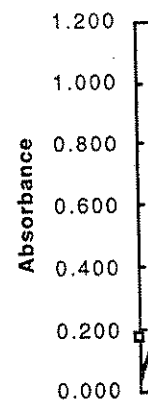
1. Start with a table of wavelength, absorbance data pairs.
2. Create a column of wavenumbers.
3. Determine the number of bands necessary to describe the spectrum. This can usually be arrived at by inspection: a strongly asymmetric band generally indicates one or more hidden bands; a band with a flat maximum indicates two strongly overlapped bands, etc. Alternatively, you can use the first derivative of the spectrum ($\Delta A/\Delta x$). Except for the most hidden shoulders, each $\Delta A/\Delta x = 0$ value indicates a band maximum.
4. Estimate the half-width of the bands by using one or more bands not overlapped by other bands. As first approximation, use this value for all bands in the spectrum
4. Set up a table of ν_{\max} , A_{\max} and σ for each band.
5. Calculate the band profile for each contributor.
6. Sum the individual band contributions.
7. Calculate the sum of squares of the residuals $(A_{\text{obsd}} - A_{\text{calc}})^2$.
8. Create an embedded chart, plotting A_{obsd} and A_{calc} .
9. Perform some manual adjustment of the parameters, attempting to make the calculated spectrum coincide with the observed. This is especially important if the spectrum is complicated (more than three or four bands, especially if they are overlapped strongly).
10. Use the Solver to minimize sum of squares of residuals by varying (ultimately) the $3N$ parameters for the N bands in the spectrum.

TACKLING A COMPLICATED SPECTRUM

For a complicated spectrum, it may be helpful to operate on a reduced-size data set. Many spectrometers record absorbance readings at 1-nm intervals; a complete UV-visible spectrum (200 to 700 nm) contains 500 data points. If the spectrum contains eight bands, you're performing calculations on more than 4000 cells. Start with a data set consisting of every 10th data point, for example. After getting a reasonably good fit to this data set, use these values as initial parameters for the complete data set.

It may be necessary to first minimize portions of the spectrum separately.

	A	
1		
2		
3		
4	(wavenum	
5	(absorba	
6	(bandwi	
7	(wavelen	
8		
9	λ , nm	
10	300	(
11	310	(
12	320	(
13	325	(
14	330	(
15	335	
16	340	
17	345	
18	350	
19	355	
20	360	
21	370	
22	380	
23	390	



	A	B	C	D	E	F	G	H	I
1	Ni(2,3,2-tet)(en)2+ spectrum								
2	(b = 5 cm, c = 0.0252 M, pH = 10.6)								
3				band1	band2	band3	band4		
4	(wavenumber)	$\tilde{\nu}_{max}$	29.25	22.72	18.56	11.69			
5	(absorbance)	A_{max}	1.12	0.15	0.87	0.77			
6	(bandwidth)	S	1.60	1.54	1.38	1.5			$\Sigma(a^2)$
7	(wavelength)	λ_{max}	342	440	539	855			0.0148
8									
9	λ, nm	Abs	$\tilde{\nu}, cm^{-1}$	band1	band2	band3	band4	Σ	d^2
10	300	0.173	33.33	0.043	0.000	0.000	0.000	0.043	
11	310	0.274	32.26	0.191	0.000	0.000	0.000	0.191	0.007
12	320	0.514	31.25	0.512	0.000	0.000	0.000	0.512	0.000
13	325	0.694	30.77	0.714	0.000	0.000	0.000	0.714	0.000
14	330	0.871	30.30	0.903	0.000	0.000	0.000	0.903	0.001
15	335	1.026	29.85	1.046	0.000	0.000	0.000	1.046	0.000
16	340	1.126	29.41	1.118	0.000	0.000	0.000	1.118	0.000
17	345	1.141	28.99	1.109	0.000	0.000	0.000	1.109	0.001
18	350	1.036	28.57	1.028	0.000	0.000	0.000	1.028	0.000
19	355	0.908	28.17	0.896	0.000	0.000	0.000	0.896	0.000
20	360	0.737	27.78	0.737	0.001	0.000	0.000	0.738	0.000
21	370	0.406	27.03	0.429	0.003	0.000	0.000	0.432	0.001
22	380	0.195	26.32	0.210	0.010	0.000	0.000	0.220	0.001
23	390	0.111	25.64	0.089	0.025	0.000	0.000	0.114	0.000

Figure 19-10. Deconvolution of the UV-visible spectrum.

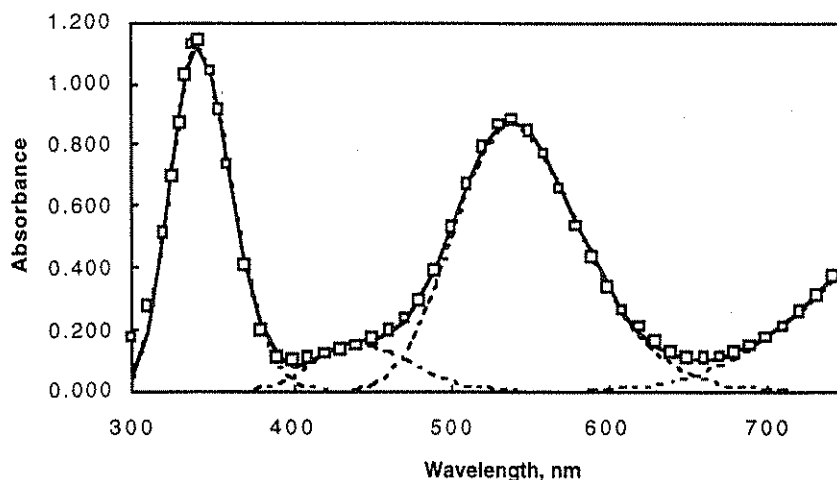


Figure 19-11. Deconvoluted spectrum.

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