Convoluting UV-Vis spectra using oscillator strengths

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In general, the absorption or emission of light by a chemical compound is accompanied by a transition of states. The energy difference between these states ΔE is related to the frequency ν , the wavelength λ and the wave number ν' of absorbed or emitted light as follows:

$$\Delta E = h\nu = hc/\lambda = hc\nu' \tag{1}$$

where h is Planck's constant and c is the speed of light.

The absorption of light by a compound in solution is defined as $A = log(I_0/I)$. This absorption is proportional to the concentration, C, and the path-length (e.g. width of the cuvette), d. This is the Beer-Lambert Law $A = \epsilon Cd$ where the constant of proportionality ϵ is referred to as the decadic molar absorption coefficient, or simply the absorptivity.

The absorptivity is a measure of the intensity of an electronic transition and how strongly it is allowed. Experimentally, bands are observed and the overall strength of an electronic transition must be evaluated by integrating over the associated band.

Next we introduce the concept of the oscillator strength of a particular electronic transition. This dimensionless quantity is defined as follows:

$$f = \frac{4m_e c\epsilon_0}{N_A e^2} B \tag{2}$$

where m_e is the mass of an electron, ϵ_0 the vacuum permittivity, N_A Avogadro's constant, e the elementary charge and B the molar natural absorption coefficient integrated over the whole band in units of frequency (from ν_1 to ν_2). The oscillator strength is a number usually between one and zero. Forbidden transitions have oscillator strengths close to zero, while bands arising from electronically allowed transitions show values of the order of one.

Rearrangement of B into terms already introduced yields:

$$B = \int_{\nu_1}^{\nu_2} \mathrm{d}\nu. \frac{\ln \frac{I}{I_0}}{Cd} = \ln 10 \int_{\nu_1}^{\nu_2} \mathrm{d}\nu. \epsilon = c \ln 10 \int_{\nu_1'}^{\nu_2'} \mathrm{d}\nu'. \epsilon \tag{3}$$

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Substituting into Equation 2 gives:

$$f = \frac{4m_e c^2 \epsilon_0}{N_A e^2} \ln 10 \int_{\nu_1}^{\nu_2} \mathrm{d}\nu' \epsilon \tag{4}$$

Theoretically (under the transition dipole length approximation), the oscillator strength can be related to the transition dipole moment, \mathbf{M} , as follows:

$$f_{i \to f} = \frac{8\pi^2 m_e}{3e^2 h^2} \Delta E_{i \to f} \left| \mathbf{M}_{i \to f} \right|^2 = \frac{8\pi^2 m_e c}{3e^2 h^2} \nu'_{i \to f} \left| \mathbf{M}_{i \to f} \right|^2 \tag{5}$$

We now look at how to use Gaussian functions to convolute calculated oscillator strengths for comparison with experimental results. Gaussian functions g(x) are of the general form:

$$g(x) = N. \exp^{-\alpha (x-\beta)^2}$$
(6)

They are centered at β , which can easily be shown by substituting $x = \beta$, yielding the maximum value $g(\beta) = N$. Their integral over the whole of space is

$$\int_{-\infty}^{\infty} \mathrm{d}x g(x) = N \sqrt{\frac{\pi}{\alpha}} \tag{7}$$

We will approximate the shape of the band profile as a Gaussian function $g(x) = \epsilon(\nu')$, i.e. the decadic molar absorption coefficient as a function of wave number. Combining Equations 4 and 5, we get:

$$\int_{-\infty}^{\infty} \mathrm{d}\nu' \epsilon(\nu') = N \sqrt{\frac{\pi}{\alpha}} = \frac{N_A e^2 f}{4m_e c^2 \epsilon_0 \ln 10} \tag{8}$$

We now introduce the parametrical value of the full-width half-maximum (FWHM) of the band given in units of ν' and symbolised by $\Delta_{1/2}\nu'$. Solving Equation 7 for this value by substituting $\epsilon(\beta \pm \frac{1}{2}\Delta_{1/2}\nu') = 1/2N$ we get:

$$\alpha = \frac{4\ln 2}{(\Delta_{1/2}\nu')^2} \tag{9}$$

With α we can now solve Equation 8 for the normalisation constant N obtaining:

$$N = \frac{N_A e^2 f}{2m_e c^2 \epsilon_0 \ln 10.(\Delta_{1/2}\nu')} \sqrt{\frac{\ln 2}{\pi}}$$
(10)

Substituting these results and $\beta = \nu'_{i \to f}$ into Equation 6 and simplifying the constants into numerical expressions gives us:

$$\epsilon(\nu') = \frac{2.175 \cdot 10^8 L.mol^{-1}.cm^{-2}}{\Delta_{1/2}\nu'} f \cdot \exp\left[-2.772 \left(\frac{\nu' - \nu'_{i \to f}}{\Delta_{1/2}\nu'}\right)^2\right]$$
(11)

This is the formula that GaussSum uses to convolute spectra. The user supplies $\Delta_{1/2}\nu'$, while the values of f and $\nu'_{i\to f}$ are derived from a quantum mechanical calculation.

References

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