Oscillator Strengths

The extinction coefficient evaluated at an absorption peak is frequently used for analytical purposes, since a knowledge of its value allows the determination of concentration by measurement of absorbance. But you will notice that the absorption peak associated with a given transition spans a range of wavelengths. The theoretical absorption intensity should therefore be compared to the integrated absorption coefficient

$$\sigma = \int_{\omega_{min}}^{\omega_{max}} \varepsilon \, d\omega$$

where ω_{max} and ω_{min} are the maximum and minimum frequencies spanned by the absorption band. The integral should have units of liters·mole^{-1}·cm^{-2}.

When evaluating theoretical and experimental values of σ be very careful to express all quantities in the correct units. To avoid confusion with units, transition intensities are usually reported in terms of the dimensionless quantity f, the oscillator strength:

$$f = \frac{2302 m_e c^2}{\pi N e^2} \sigma = (4.32 \cdot 10\text{-}9 \text{ moles·cm}^2\text{·liter-}1)\,\sigma$$

For transitions out of the ground state, values of the oscillator strength range from approximately 1.0 for strong transitions to 0.0 for forbidden transitions.

$$\nu = \frac{c}{\lambda}$$

$$f = 4.3 \cdot 10^{-9} \cdot \varepsilon_0 \int e^{-6(\lambda_{max} - \lambda)^2} d\left(\frac{c}{\lambda}\right) =$$

$$= 4.3 \cdot 10^{-9} \cdot \varepsilon_0 \cdot c \int e^{-6(\lambda_{max} - \lambda)^2 / \lambda^2} \, d\lambda$$

$$\| \quad 10^7$$

$$= 4.3 \cdot 10^{-2} \, \varepsilon_0 \cdot \int \frac{e^{-6(\lambda_{max} - \lambda)^2}}{\lambda^2} \, d\lambda$$