

#### 10.3.6.4 Factors affecting luminescence data

##### *10.3.6.4.1 Geometric arrangement of sample*

The luminescence measured may depend on the directions of the exciting and emitting beams with respect to the sample. The angles relating to excitation and emission directions can be expressed by two figures,  $\alpha$ ,  $\beta$ , where  $\alpha$  = angle of incidence of the exciting beam on the plane surface of the sample, and  $\beta$  = angle between the exciting direction and observation direction. *Front surface geometry* is defined as a system where excitation and observation are from the same face of the sample ( $\alpha < 90^\circ$ ,  $\beta < 180^\circ$ ).

TABLE 10.15 Selected terms, symbols and units summarised from Chapter 10, relevant to spectrochemistry and from Chapter 11, relevant to light scattering and photochemistry

Terms	Symbols	Practical Units	Notes
(radiant) energy	$Q$	J	
radiant energy (spectral)	$Q_\lambda$	$\text{J nm}^{-1}$	$=dQ/d\lambda$
radiance	$L$	$\text{W m}^{-2} \text{sr}^{-1}$	
radiance (spectral)	$L_\lambda$	$\text{W m}^{-3} \text{sr}^{-1}$	
radiant energy density	$\rho, w$	$\text{J m}^{-3}$	
radiant power (spectral)	$\varphi_\lambda$	$\text{W nm}^{-1}$	
radiant power (incident)	$\varphi_0$	W	
radiant power (transmitted)	$\varphi_\tau$	W	
radiant power (absorbed)	$\varphi_a$	W	
radiant exposure	$H$	$\text{J m}^{-2}$	
radiant exitance	$M$	$\text{W m}^{-2}$	radiant flux emitted
irradiance	$E$	$\text{W m}^{-2}$	radiant flux received
irradiance (spectral)	$E_\lambda$	$\text{W m}^{-3}$	
transmittance	$\tau$	1	
internal transmittance	$\tau_i$	1	
reflectance	$\rho$	1	$=\varphi_r/\varphi_0$
absorptance	$\alpha$		
internal absorptance	$\alpha_i$	1	$=\varphi_a/\varphi_0$
spectral responsivity	$S_\lambda$		
wavelength modulation interval	$\Delta\lambda_{\text{mod}}$	nm	
bandgap energy	$E_g$	$\text{J mol}^{-1}$	
Fermi level	$E_f$	$\text{J mol}^{-1}$	
fluence	$H_0$	$\text{J m}^{-2}$	
fluence rate	$E_0$	$\text{W m}^{-2}$	
frequency (linear)	$\nu$	Hz	
frequency (angular)	$\omega$	$\text{rad s}^{-1}$	
oscillator strength	f number	1	
lifetime	$\tau$	s	
Rayleigh ratio	$R_w, R_v, R_h$		
real refractive index	$n$		
refractive index			
relative refraction index	$m$		
permittivity	$\epsilon$		

Terms	Symbols	Practical Units	Notes
relative permittivity	$\epsilon_r$		
scattering angle	$\theta$		
Stokes parameters	$S_0^0, S_1^0, S_2^0, S_3^0$		
transition dipole moment	$M^{nm}$	Cm	
spectral overlap integral (Förster)	$J$	$\text{m}^6 \text{mol}^{-1}$	
quantum yield	$\phi$		
energy yield of fluorescence (phosphorescence, delayed fluorescence)	$Y_{\text{cf(P,DF)}}$	1	
quantum efficiency of fluorescence (phosphorescence)	$\eta_{\text{F(P)}}$	1	
lifetime of fluorescence (phosphorescence, delayed fluorescence)	$\tau_{\text{F(P,DF)}}$	s	
dissociation constant (acid-base) of molecule in first excited single state (= $c_{\text{H}^+}c_{\text{A}^*}/c_{\text{HA}^*}$ in equilibrium at temperature T)	$K_{\text{aS}}^*$	$\text{mol}^{-1}$	
dissociation constant (acid-base) of molecule in lowest triplet state (= $c_{\text{H}^+}c_{\text{A}^*}/c_{\text{HA}^*}$ in equilibrium at temperature T)	$K_{\text{aT}}^*$	$\text{mol}^{-1}$	
radiant intensities of the beam resolved into directions parallel and perpendicular to the direction of polarization of the exciting radiation	$I_{\parallel}, I_{\perp}$		
degree of polarization	$P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$		
degree of polarization (corrected for depolarizing factors)	$P_0$	1	
degree of depolarization or dichroic emission ratio	$D = I_{\parallel} / I_{\perp}$	1	
degree of anisotropy	$r = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + 2I_{\perp})$		

#### *10.3.6.4.2 Pre-filter, post-filter and self-absorption effects*

The *pre-filter effect* arises when the luminescence detector does not see a portion of the luminescent volume where the excitation beam enters the sample. Thus, the exciting beam flux is reduced by absorption by the analyte and interfering impurities before it enters the volume observed by the detection system.

The *post-filter effect* arises when the exciting beam does not fill the cell completely and luminescence is absorbed by the analyte and interfering impurities in the non-illuminated region facing the detector.

The *self-absorption effect* is the reabsorption of luminescence by the analyte and interfering impurities within the excitation volume.

All these effects are minimized if front surface geometry is used and/or the solution is highly diluted.

#### *10.3.6.4.3 Refraction effects*

The luminescence flux emitted from the interior of a rectangular sample reaching a photodetector placed at some distance from the sample is decreased by a factor of approximately  $n^2$  (where  $n$  is the refractive index of the medium) compared with a medium whose refractive index is 1.0. Such effects are termed *refraction effects*.

#### *10.3.6.4.4 Solvent and temperature effects*

The type of solvent and its temperature can effect the luminescence yield from an analyte as a result of quenching, exciplex formation, aggregation, etc. *Temperature effect* is the term used for changes in the luminescence parameters caused by changes in temperature, while *solvent effects* are changes caused by altering the solvent or the solvent properties.