10.2.1.1 Optical radiation

10.2.1.1.1 Atomic and ionic spectral lines

Atomic- and *ionic spectral lines* originate from specified electronic transitions between *energy levels* of atoms and ions, respectively. That lines are due to atomic or ionic transition respectively is expressed thus:

Element symbol I wavelength e.g. Cu I 324.7 nm;   and
Element symbol II wavelength e.g. Cu II 213.6 nm

Similarly, for higher states of ionization, the type of line is represented by III, IV etc.

TABLE 10.1   Nomenclature & Symbols Relating to Radiant Energy

	I Name	II Symbol	III Definition	IV Dimensions	V SI unit	VI Practical Unit
1	radiant flux or radiant power	ϕ	dQ/dt	power	W	W
2	energy	Q	$Q = \int_1^0 \phi dt$	energy	J	$W\,s = J$
3	radiant intensity	I	$l = \phi/\omega$	$\dfrac{power}{solid\ angle}$	$W\,sr^{-1}$	$W\,sr^{-1}$
4	radiance	$B \dots L$	$B = \dfrac{\phi}{S\omega\cos\xi}$	$\dfrac{power}{solid\ angle * area}$	$W\,sr^{-1}\,m^{-2}$	$W\,sr^{-1}\,cm^{-2}$
5	emissivity	J	$J = \dfrac{f}{V\omega}$	$\dfrac{power}{solid\ angle * volume}$	$W\,sr^{-1}\,m^{-3}$	$W\,sr^{-1}\,cm^{-3}$
6	energy density	u	$u = Q/V$	$\dfrac{energy}{volume}$	$J\,m^{-3}$	$J\,cm^{-3}$
7	irradiance	E	$E = \phi/S$	$\dfrac{power}{area}$	$W\,m^{-2}$	$W\,cm^{-2}$
8	exposure	H	$H = \int_0^1 Edt$	$\dfrac{power * time}{area}$	$J\,m^{-2}$	$W\,s\,cm^{-2} = J\,cm^{-2}$

Note to 3 to 8: It must be kept in mind that the basic quantity in this system, the radiant flux ϕ, may vary in space and direction. Therefore the area S, the solid angle ω and the volume V in the defining equations 3 to 8 must be small enough to give meaningful local values for the derived quantities.

Note to 4,7 and 8: S refers to the area of the radiating element for the term radiance, and to the area of the irradiated element for the terms irradiance and (radiant) exposure: ε is the angle between the normal to the surface and the direction of the radiating beam, which is assumed to be confined to a narrow solid angle.

Note to 4: The old symbol B is recommended for radiance in contradiction to IUPAC 1970 [*Pure Appl. Chem.* **21**, 1 (1970)], which only lists L. the letter L should not be used for radiance in atomic emission spectroscopy, since L is also the symbol for the spectrum line, for the orbital quantum number and also for self-inductance.

Note to 7 and 8: The letter E may logically be expected as a symbol for the radiant exposure. However, E has been internationally adopted for irradiance while H was chosen as symbol for exposure. Both quantities are important in photographic photometry, but they are seldom used in the practice of spectrochemcial analysis.

Note to 2,5,6 and 8: In these cases the adjective radiant may be omitted, if the meaning of the term is clear from the context. Radiant should not be dropped from radiant flux and radiant intensity.

Note to 4,5,6,7 and 8: For the practical units it is proposed to use the centimetre as a unit of length. The reason for this proposal is obvious: the dimensions of most radiant sources used in spectroscopy are of the order of a centimetre. The use of this unit therefore helps visualization.

10.2.1.1.2 Continuous radiation

Continuous radiation (*continuum*) arises from non-quantified *free-free transitions* of electrons in the fields of the ions, *free-bound transitions* or *radiative recombinations* of electrons and ions, *incandescent radiation* emitted by hot solids (when the radiation distribution conforms to that described by *Planck's law*, it is considered black body radiation) and *unresolvable band spectra*, i.e., where the *widths* of the spectral lines are wider then the spacings between them.

10.2.1.1.3 The shape and shift of spectral lines

The shape of a spectral line is described by the *line profile function* and its width by its *full width at half maximum* intensity (*peak intensity*) (FWHM). The *physical line shape* is due to the combined effects of the different *broadening processes*. The physical shape described by the *Voigt function* is known as the *Voigt profile* and takes into account natural broadening, Doppler broadening and pressure broadening. *Line shift* is the displacement of the central wavelength of the spectral line by similar effects.

Natural broadening has its origin in the finite optical lifetime of one or both levels involved in the transition.

Doppler broadening is due to the random motion of the emitting or absorbing atoms. A Doppler broadened line has a *Gaussian shape*.

A *Doppler shift* is a line shift caused by the Doppler effect.

Collisional broadening and *collisional shift* of the line is produced by collisions of the emitting or absorbing particle with other particles. When collisions occur between unlike, neutral particles, we use the term *foreign-gas broadening*. When the colliding particles are of the same species, we speak of *resonance broadening*.

When collisions take place with charged particles or particles with a strong permanent electrical dipole moment, we speak of *Stark broadening*. A strong chaotic electrical field causes Stark broadening, whereas an applied static electrical field induces a *Stark shift*.

Photons emitted in one region of a source are partly absorbed in their passage through the plasma. Because the *absorption profile* is of the same shape as the *emission profile*, energy is selectively absorbed from the emission line, i.e., the *absorption coefficient* is a maximum at the centre of the line or central wavelength. The actual line profile is changed as a result of the lowering of the maximum intensity accompanied by a corresponding increase in apparent halfwidth. This is termed *self-absorption broadening*.

Self-reversal is a case of *self-absorption*, when a line is self-absorbed to such an extent that the peak or central wavelength intensity is less than at the wings of non-central wavelengths.

The *Zeeman effect* arises when atoms are exposed to a magnetic field. Such a field splits the energy levels resulting in a separation of the spectral lines into several components.

10.2.1.1.4 Polarization

Radiation from sources may be *polarized*. This radiation may be *plane*, *circularly* or *elliptically polarized*.

10.2.1.1.5 Scatter

Radiation may be scattered by its transmission through a medium containing particles. If the scatter results in no significant change in the wavelength relative to the primary radiation, it is called *elastic scattering*. In cases where the scattering centres are small compared to the wavelength of the radiation, the elastic scattering is called *Rayleigh scattering* and is termed *Mie scattering* if this condition is not fulfilled. If the scattering process causes a wavelength change, it is *inelastic scattering*. *Raman scattering* is a case of inelastic scattering.