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SOLAR IRRADIANCE

The Effect of Dimensionality on Solar Spectrum Curves

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ABSTRACT

The shape of the solar irradiance curve and the location of its maximum are dependent upon the units chosen for expressing irradiance and therefore upon the experimental method of making the measurements. Some of the confusion resulting from this fact could be eliminated if relative bandwidth were used instead of the more conventional wavelength bandwidth or wavenumber bandwidth. Formulae are given and curves are shown for expressing solar irradiance (6000° K black body) in all three ways and with respect to both power and photon rate.

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The well-known Wien displacement law, which was obtained in 1896 by the application of thermodynamic considerations to black body radiation, states that the product of the absolute temperature, T , and the wavelength of maximum emission of a black body is a constant:

$$\lambda_{\max} \cdot T = w$$

Wien's constant, w , is often given as $0.290 \text{ cm}^{\circ}\text{K}$ or $2.90 \times 10^6 \text{ nm (nanometers)}^{\circ}\text{K}$. This implies that the maximum emission of the sun, whose surface closely approximates a black body at 6000°K , comes at 483 nm . The significance of this value with respect to the evolution of our visual apparatus and its peak sensitivity in that region of the spectrum has often been discussed. It is less well-known, however, that the value of the constant, w , depends crucially upon how the emitted radiation is measured. The above value of $2.90 \times 10^6 \text{ nm}^{\circ}\text{K}$ applies only for power emitted per unit area per unit wavelength of spectral bandwidth. The black body emission spectrum for 6000°K and a fixed wavelength of spectral bandwidth is shown in Figure 1.

If, instead of unit wavelength, we express the intensity as power per unit area per wavenumber of spectral bandwidth, the same black body emission gives the spectrum shown in Figure 2 with a maximum at 850 nm ! Wien's law still applies for the shift in $\lambda_{\max}$ with T but the constant, w , is now $5.10 \times 10^6 \text{ nm}^{\circ}\text{K}$. This apparent anomaly in the position of the solar emission maximum has led to misunderstanding and much meaningless invective about which part of the solar spectrum is most important

if the aim is to store solar energy. One can justify working with porphyrins as sensitizers by invoking the power spectrum at constant wavelength increment ($\lambda_{\text{max}} = 483 \text{ nm}$). If one prefers research in the near infrared then one cites the spectrum with constant wavenumber increment, which has λ_{max} at 850 nm. Instead of power, if we use number of photons per second, which is more relevant in photochemistry, there are two other representations of the solar spectrum commonly given. Photon flux per unit wavelength interval (Figure 3) gives a maximum at 612 nm, fairly close to the chlorophyll absorption maximum, while photon flux per unit wavenumber interval (Figure 4) peaks at 1503 nm (1.5 microns), which is in the overtone region of vibrational excitation. All four of these spectra are equally valid representations of black body emission at 6000° K , as shown in the Appendix.

This is not an entirely frivolous discussion. It applies to any emission measurement, for example fluorescence emission. The point of maximum emission, which is usually the only quantity reported in the text of a scientific article, depends on how the spectral bandwidth of the fluorimeter depends upon spectral position. The essential point to realize is that, while the peak position is a matter of personal preference, the areas under the power curves (Figures 1 and 2) between any two specified spectral positions are equal, as they must be, because both integrals have the same units, i.e., power per unit area. Likewise, the areas under the photon flux curves are also equal. In terms of finite intervals and integrals, therefore, one can, in fact, make precise statements about power or photon flux in various regions of the black body spectrum. It is only the intensity distribution curves

themselves, which are in differential form, that depend on the method chosen arbitrarily for differentiation.

The scales on Figures 1 and 2 are adjusted so that equal areas on the figures themselves represent equal quantities of irradiance in power per unit area. Similarly Figures 3 and 4 are adjusted to have equal areas under them correspond to equal numbers of photons per second per unit area.

One good way to remove the apparent anomaly among emission spectra is to plot intensity per unit relative wavelength, $d\lambda/\lambda$, or relative wavenumber, $d\omega/\omega$. Since $d\omega/\omega = -d\lambda/\lambda$ the plots become identical whether wavelength or wavenumber units are used. The abscissa should then be made linear in $\ln \lambda$ to give the integrals the proper units of power per unit area and photons per second per unit area. Such plots are shown in Figures 5 and 6. As can be seen in the Appendix, these curves, except for dimensionality and scaling factor, turn out to be the same as those in Figures 3 and 2. This latter choice of coordinates for plotting emission spectra, while admittedly a matter of taste, has the advantage that there is only one relative wavelength (or frequency) scale and that is the logarithmic one. Thus, comparisons among emission phenomena in widely different portions of the electromagnetic spectrum can be made in the same units whether experiments are conventionally done using Angstroms, nanometers, microns, Hertz, wavenumbers, or whatever.

In all the Figures, the units of solar irradiance have been adjusted for the distance of the earth from the sun's 6000° K black body surface. For an irradiance of W watts cm^{-2} , the total power radiated from the sun is $4\pi(R_S)^2$, where R_S = the sun's radius. At the distance of

the earth, R_E , this power is isotropic over an area $4\pi(R_E)^2$. Thus the irradiance at the earth is $W(R_S/R_E)^2$ or 2.2×10^{-5} W.

Appendix

The radiant power per unit wavelength of spectral bandwidth of a black body into a solid angle of 2 steradians is called the spectral exitance and is given by Planck's equation as

$$(1) \quad W_{\lambda} = 2\pi hc^2 \lambda^{-5} (e^x - 1)^{-1}, \text{ where } x = hc/\lambda kT$$

The power per unit area emitted between two wavelengths, λ_1 and λ_2 , is therefore

$$(2) \quad \int_{\lambda_1}^{\lambda_2} W_{\lambda} d\lambda$$

If we set $b = hc/kT$ then $x = b/\lambda$ and W can be expressed as

$$(3) \quad W_{\lambda} = 2\pi hc^2 b^{-5} x^{-5} (e^x - 1)^{-1}$$

where all of the wavelength dependence is contained in the dimensionless quantity, $x^5 (e^x - 1)^{-1}$. (At 6000° K , $b = 2.40 \times 10^{-4} \text{ cm.}$)

$(W_{\lambda})_{\text{max}} = 1.00 \times 10^{15}$ in c.g.s. units ($\text{erg sec}^{-1} \text{ cm}^{-2} \text{ cm}^{-1}$) and comes at 483 nm.

Now if we wish to express the radiant power per unit wavenumber of spectral bandwidth we use the relation

$$(4) \quad \int_{\lambda_1}^{\lambda_2} W_{\lambda} d\lambda = \int_{\omega_1}^{\omega_2} W_{\omega} d\omega$$

and make the substitution, $\lambda = 1/\omega$ and $d\lambda = -\lambda^2 d\omega$. Thus,

$$(5) \quad W_{\omega} = \lambda^2 W_{\lambda} \quad (\text{The sign can be ignored.})$$

To express emission in terms of photon flux per unit wavelength spectral bandwidth we simply divide W_{λ} by the photon energy, hc/λ .

$$\eta_{\lambda} = (\lambda/hc) W_{\lambda}$$

For photon flux per unit wavenumber spectral bandwidth, we get similarly,

$$(6) \quad \eta_{\omega} = (\lambda^3/hc) W_{\lambda}$$

Finally, to express radiant power in terms of relative wavelength interval we note

$$(7) \quad W_{\lambda} d\lambda = W_{\ln} (d\lambda/\lambda) = W_{\ln} d\ln\lambda$$

from which

$$(8) \quad W_{1n} = \lambda W_{\lambda}$$

Likewise

$$(9) \quad \eta_{1n} = \lambda \eta_{\lambda} = (\lambda^2/hc) W_{\lambda}$$

Using the relations (4) through (9) and making conversions to the dimensionless quantity, x , we get the set of equations shown in Table 1 that describe the functions plotted in Figures 1 through 6.

The scales of the Figures are normalized so that equal areas under the curves represent equal quantities of watts cm^{-2} (Figures 1,2,5) and of photons $\text{sec}^{-1} \text{ cm}^{-2}$ (Figures 3,4,6).

The numerical values of the ordinates are adjusted, as explained in the text, to give actual intensities at the top of the earth's atmosphere rather than at the black body surface of the sun.

TABLE 1.

Black Body Emission Functions (Spectral Exitance)

<u>Figure No.</u>	<u>Function</u>	<u>Plotted vs.</u>
1.	$W_{\lambda} = 2\pi hc^2 b^{-5} \cdot x^5 (e^x - 1)^{-1}$ erg.sec ⁻¹ · cm ⁻² · cm ⁻¹	λ
2.	$W_{\omega} = 2\pi hc^2 b^{-3} \cdot x^3 (e^x - 1)^{-1}$ erg.sec ⁻¹ · cm ⁻² · (cm ⁻¹) ⁻¹	ω
3.	$\eta_{\lambda} = 2\pi c b^{-4} \cdot x^4 (e^x - 1)^{-1}$ photon · sec ⁻¹ · cm ⁻² · cm ⁻¹	λ
4.	$\eta_{\omega} = 2\pi c b^{-2} \cdot x^2 (e^x - 1)^{-1}$ photon · sec ⁻¹ · cm ⁻² · (cm ⁻¹) ⁻¹	ω
5.	$W_{\ln} = 2\pi hc^2 b^{-4} \cdot x^4 (e^x - 1)^{-1}$ erg.sec ⁻¹ · cm ⁻²	$\ln \lambda$
6.	$\eta_{\ln} = 2\pi c b^{-3} \cdot x^3 (e^x - 1)^{-1}$ photon · sec ⁻¹ · cm ⁻²	$\ln \omega, \ln \lambda$

$$b = hc/kT$$

$$x = hc/\lambda kT$$

$$= 2.40 \times 10^{-4} \text{ cm at } 6000^{\circ}\text{K}$$

FIGURE 1

SOLAR IRRADIANCE
POWER VS. WAVELENGTH

FIGURE 2

SOLAR IRRADIANCE
POWER VS. WAVENUMBER

FIGURE 3

SOLAR IRRADIANCE
PHOTON RATE VS. WAVELENGTH

FIGURE 4

SOLAR IRRADIANCE
PHOTON RATE VS. WAVENUMBER

FIGURE 5

FIGURE 6

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