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Guest Commentary

Conversion of Wavelength and Energy Scales and the Analysis of Optical Emission Spectra

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The analysis of spectra is not excepted from misunderstandings. Here we draw attention to the fact that appropriate presentation and interpretation of spectral data is fundamental in scientific work. Often, it is necessary to convert an optical continuous emission spectrum measured as a function of light wavelength into one represented as a function of photon energy. This transformation has significant effects that we often do not think about. We show that it is not correct to calculate the average wavelength using the average energy obtained from the energy spectrum. Instead, the average of the energy inverse must be used. In the same way, the wavelength of maximum spectral intensity must be calculated from the value of the energy inverse for which that function is maximal. The blackbody radiance spectrum was used as the case study, although the presented results can be generalized for spectral distributions of any kind.

The graphical representation of data plays a fundamental role in scientific communication. The same data can be represented graphically in different ways. For example, an optical continuous emission spectrum is often represented as a

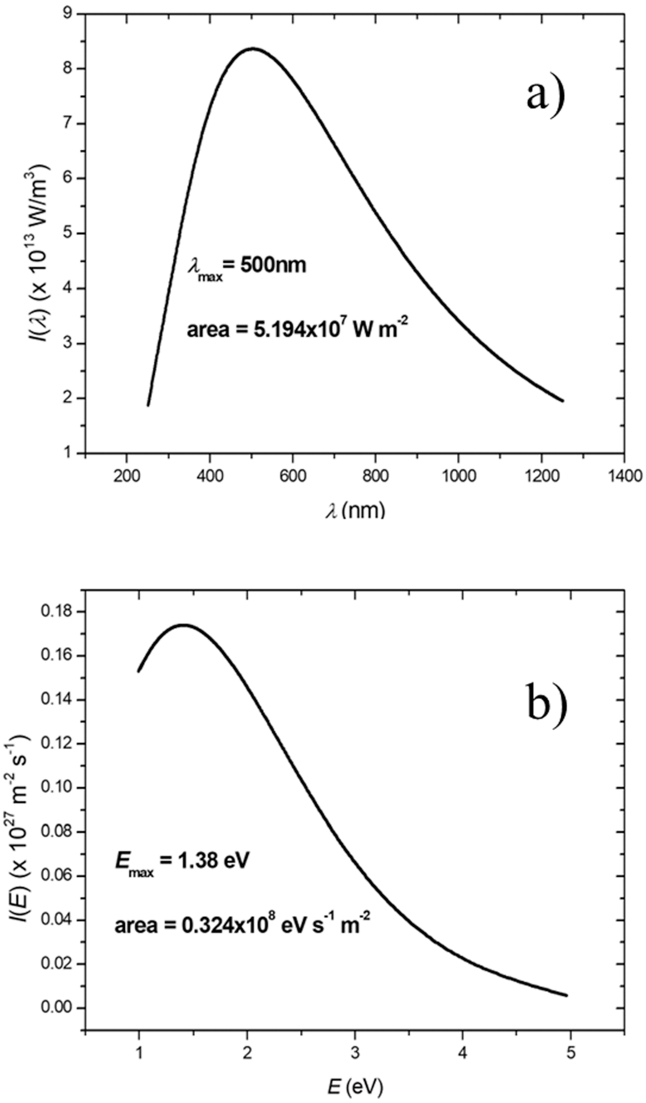

Figure 1. $I(\lambda)$ as a function of λ (a) (eq 9) and $I(E)$ as a function of E (b) (eq 10) for T = 5800 K. The values of wavelength and energy at which the radiances are maximal and the areas under the curves are shown in the insets.

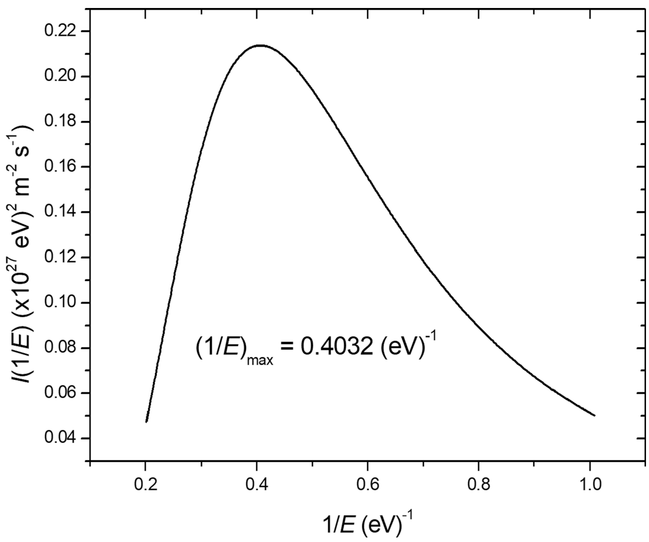

Figure 2. Radiance $I(1/E)$ as a function of $1/E$ (see eq 11) for a blackbody at T = 5800 K. The abscissa's axis value for which the curve's maximum appears is shown in the legend.

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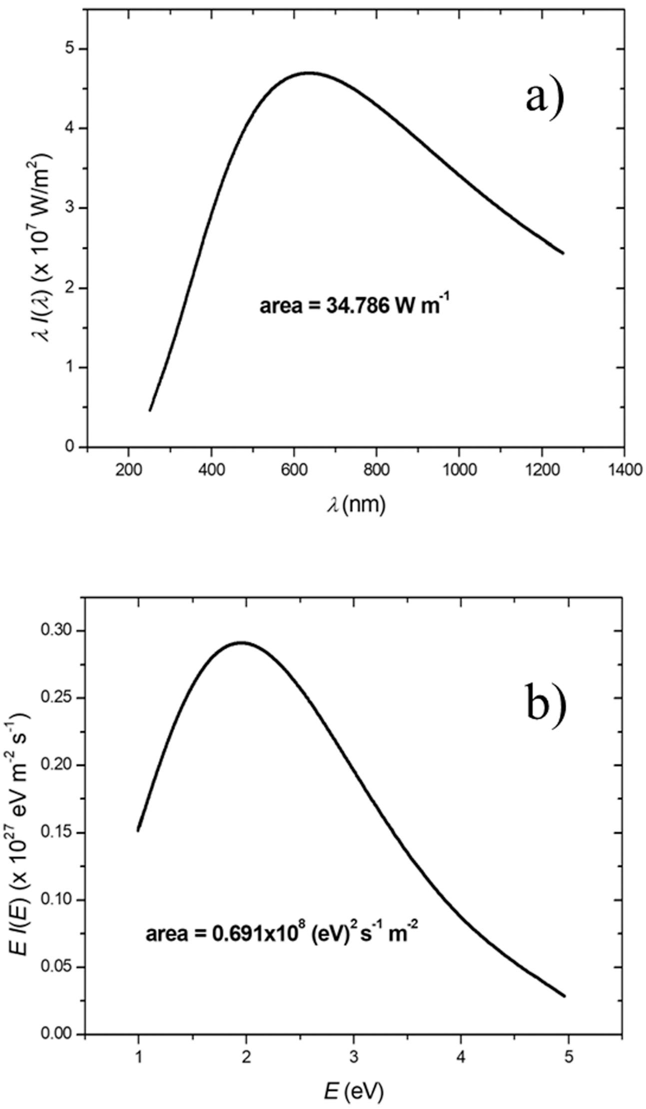

Figure 3. $\lambda I(\lambda)$ as a function of λ (a) and $EI(E)$ as a function of E (b) for T = 5800 K. The areas under the curves are shown in the legends.

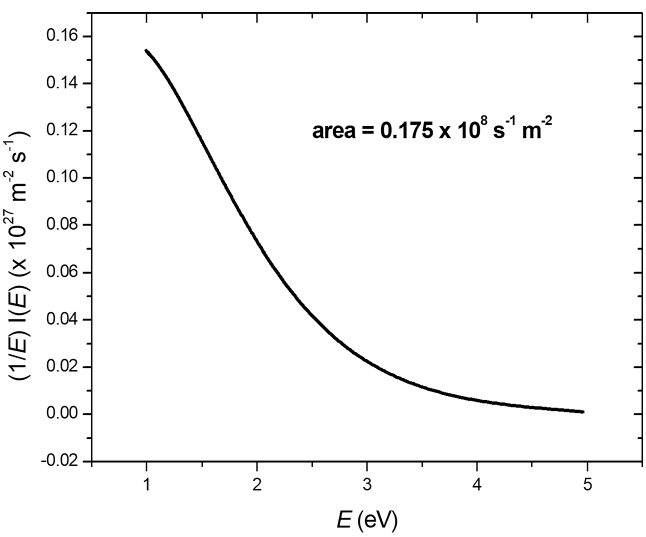

Figure 4. $(1/E)I(E)$ versus E for T = 5800 K. The legend shows the area under the curve.

graph of the electromagnetic radiation's spectral intensity, $I(\lambda)$, as a function of wavelength, λ. In this case, the spectral intensity is defined as the amount of light energy (number of photons times the energy of each photon) reaching a detector per time unit, per unit area, and per wavelength increment interval, dλ. In other words, spectral intensity is intensity per wavelength interval.[1] The function $I(\lambda)$ is expressed in units of Wm^{-3}. But the spectral intensity can also be shown as a function of other quantities. In this paper, we will take the photon's energy as an example of one of these quantities. However, the following analysis can also be applied for parameters such as the frequency, $\nu = c/\lambda$ (where c is the speed of light in vacuum), the wavenumber ($k = 2\pi/\lambda$), etc. The wavelength is related to the energy by

$$\lambda = \frac{hc}{E} \tag{1}$$

where h is Planck's constant and hc = 1240 eV·nm = 1.986 × 10^{-25} J·m.

In many cases, converting a spectrum measured as a function of λ into one graphed versus E is necessary. The spectral intensity, $I(E)$, will be defined as the amount of light energy measured per time unit, per unit area, and per energy increment interval, dE. Then, the units of $I(E)$, $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$, differ from those of $I(\lambda)$. It is not enough to simply substitute λ with E using eq 1 to convert $I(\lambda)$ into $I(E)$. The reason is simple but often goes unnoticed by students, teachers, and even scientists: the areas under the spectral intensities' curves represent the total radiated energy fluxes that must be the same, independent of whether they are measured as a function of λ or of E (a graphical illustration of this can be found elsewhere[2]). Obviously, if we change the values and units of the abscissa axes keeping the ordinate axes identical, both absolute values and the units of these areas will differ. To overcome this, an additional transformation is needed to be applied to the spectral intensity as follows:

Following the above definitions, the law of conservation of energy reads

$$I(\lambda)\,\mathrm{d}\lambda = I(E)\,\mathrm{d}E \tag{2}$$

Combining eqs 1 and 2, one obtains[2]

$$I(E) = I(\lambda)\frac{\mathrm{d}\lambda}{\mathrm{d}E} = I(\lambda)\frac{\mathrm{d}}{\mathrm{d}E}\left(\frac{hc}{E}\right) = -I(\lambda)\frac{hc}{E^2} \tag{3}$$

Of course, for the right transformation, in the argument of the function $I(\lambda)$ the wavelength must be converted to energy using eq 1. Now, the areas under the spectral intensities' curves will acquire the same units of $\mathrm{W\,m}^{-2}$ when they are represented in terms of λ or E. The above tells us that to correctly convert a graph of $I(\lambda)$ versus λ in one of $I(E)$ versus E, not only should the scale of the abscissa's axis be converted using eq 1, but the scale of the ordinate's axis should be scaled into the factor hc/E^2 according to eq 3. This operation is called a Jacobian transformation. Equation 6 says that the Jacobian dλ/dE transforms $I(\lambda)$ into $I(E)$.

Notice that this transformation does not have to be applied whenever a quotient between intensities is made because the transformation factor cancels out. For example, when the optical absorbance is calculated from an optical transmission spectrum, a quotient between the intensity of the incident light and that of the transmitted one is used. In this case, the

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absorbance value must be preserved during a conversion of the abscissa axis from wavelength to energy or vice versa.

The Jacobian transformation has significant practical effects that we often do not think about. For example, for many applications, it is important to know the quantum yield of fluorescence of a luminescent dye, and its precise measurement requires the measurement of the average wavelength of the fluorescence spectrum.[3] Sometimes people, when looking at eq 1, mistakenly think that the same average wavelength value $\langle\lambda\rangle$ obtained from an $I(\lambda)$ spectrum can be determined as $hc/\langle E\rangle$ from the average energy, $\langle E\rangle$, of the corresponding $I(E)$ spectra. This is not the case, and the reason is explained as follows.

The average wavelength is defined as

$$\langle\lambda\rangle = \frac{\int \lambda I(\lambda)\mathrm{d}\lambda}{\int I(\lambda)\mathrm{d}\lambda} \tag{4}$$

Using eq 2, we get

$$\langle\lambda\rangle = \frac{\int \frac{hc}{E} I(E)\mathrm{d}E}{\int I(E)\mathrm{d}E} = hc\langle 1/E\rangle \tag{5}$$

where $\langle 1/E\rangle$ represents the average of the energy inverse, which is not the same as the inverse of the energy average value. The limits of integration in the above equations will be defined by the spectral wavelength and energy ranges used. It is important to note that the minus sign in eq 3 reflects the different directions of integration in energy and wavelength.

Notice that $\langle\lambda\rangle$ would approximately coincide with $hc/\langle E\rangle$ only for very narrow emission spectra (e.g., for a Delta-function-like spectral distribution, we have strictly $\langle 1/E\rangle = 1/\langle E\rangle$), but for spectra with broad emission bands, eq 5 must be used. This is consistent with the well-known fact that the Jacobian transformation given by eq 3 significantly alters the shape of a broad emission spectrum. However, its effect in the shape of a narrow spectrum emitted, for example, by a dye laser (DL) or by a semiconductor nanocrystal (NC) is minimal, as shown by Mooney and Kambhampati[2] based on experimental data. It is worth noting that not only the shapes can or cannot be affected by the Jacobian transformation. If only the abscissas are transformed, then the areas under the spectral curves would always be altered because of the measurement unit-related reasons mentioned before. These area-alterations cannot be appreciated in Figure 2 of ref 2 because the ordinate axes are shown there in arbitrary units and because the intensity values must have been normalized so that the maxima of the original and the transformed DL and NC peaks match. This is another reason why it is erroneous to omit doing the Jacobian transformation, even for a very narrow spectrum.

Let us now consider a symmetrical shaped spectral intensity distribution, say $I(\lambda)$, for which the average wavelength coincides with the wavelength of maximum emission, λ_{max}. For such a symmetrical function, from eq 5 we can deduce that

$$\lambda_{max} \neq hc/E_{max} \tag{6}$$

where E_{max} is the energy corresponding to the maximum of $I(E)$. But to arrive at eq 5 we made no assumptions about the shape of the spectral intensity nor on the symmetry of that distribution function so that the inequality in eq 6 can be generalized for spectral distributions with any shape. Therefore, in analogy to eq 5, one can propose that the wavelength of maximum spectral intensity must be calculated from the value of $1/E$ for which the spectral intensity has a maximum, namely $(1/E)_{max}$, as

$$\lambda_{max} = hc\left(\frac{1}{E}\right)_{max} \tag{7}$$

To calculate $(1/E)_{max}$, we need to do a transformation of the graph of $I(\lambda)$ versus λ into one of $I(1/E)$ versus $1/E$. One more time, to do this correctly, not only should the scale of the abscissa's axis be converted, but also the scale of the ordinate's axis should be scaled using the corresponding Jacobian transformation. Now, because energy conservation implies that $I(\lambda)\,\mathrm{d}\lambda = I(1/E)\,\mathrm{d}(1/E) = I(1/E)\,\mathrm{d}\lambda/hc$, then

$$I(1/E) = I(\lambda)hc \tag{8}$$

In this case, the Jacobian $\mathrm{d}\lambda/\mathrm{d}(1/E) = hc$ transforms $I(\lambda)$ into $I(1/E)$ through the multiplication of the ordinate's axis by the factor hc. Here again, for the right transformation, the wavelength in the argument of the function $I(\lambda)$ must be converted to energy using eq 1. Unlike the Jacobian transformation of $I(\lambda)$ into $I(E)$, for which the Jacobian factor depends on energy, the shape of the spectral intensity is preserved in the transformation of $I(\lambda)$ into $I(1/E)$ because of the constancy of the Jacobian parameter hc.

Blackbody radiation is a typical example that shows the noncoincidence between the λ_{max} value calculated from a wavelength spectrum and that obtained from the energy spectrum using the relationship $\lambda_{max} = hc/E_{max}$.[4,5] Let us consider a blackbody at an absolute temperature equal to 5800 K, for which the radiated spectrum is like that emitted by our Sun and that we would measure on Earth if we do not consider some modifications caused by the Earth's atmosphere. The spectral intensity (usually named the radiance) of a blackbody at a temperature T as a function of wavelength can be written as[6]

$$I(\lambda) = \left(\frac{c}{4}\right)\left(\frac{8\pi hc}{\lambda^5}\right)\frac{1}{(\exp(hc/\lambda k_B T) - 1)} \tag{9}$$

where k_B is the Boltzmann constant.

Using the procedure implicit in eq 2, this expression can be rewritten as a function of energy as

$$I(E) = \left(\frac{c}{4}\right)\left(\frac{8\pi E^3}{(hc)^3}\right)\frac{1}{(\exp(E/k_B T) - 1)} \tag{10}$$

These functions are graphed in Figure 1 in the UV−vis−NIR region between 250 and 1250 nm (∼1−5 eV) for T = 5800 K.

As we can see, if we plot the spectral intensity as a function of wavelength, the maximum of the spectrum will appear at λ_{max} = 500 nm, in the visible region of the electromagnetic spectrum; however, the maximum of the energy spectrum will appear at E_{max} = 1.38 eV, which would correspond to a wavelength equal to 898 nm if calculated using λ_{max} = 1240 eV/E_{max}. This value is within the near-infrared. However, following the discussion above, the wavelengths for maximal emission must be the same if the right calculation procedure is used. In what follows, the usefulness of eq 6 will be demonstrated in a graphical way.

Applying eq 8, eq 9 can be rewritten in the following way:

$$I(1/E) = \left(\frac{c}{4}\right)\left(\frac{8\pi}{(hc)^3(1/E)^5}\right)\frac{1}{(\exp(E/k_B T) - 1)} \tag{11}$$

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Equation 11 is graphed in Figure 2.

One can see that the maximum of $I(1/E)$ appears at a value of $(1/E)_{max}$ = 0.4032 $(eV)^{-1}$. Using eq 7 we obtain a value λ_{max} = 500 nm, in agreement with the value obtained from Figure 1a. In conclusion, the wavelength of maximum radiance for a blackbody at a given temperature is the same regardless of whether the radiance is plotted as a function of wavelength or if it is transformed and plotted versus the energy.

Finally, let us analyze what is happening with the average values.

Figure 3a shows a graph of $\lambda I(\lambda)$ versus λ. Following eq 4, we can say that the quotient of the areas under the curves of Figures 3a and 1a gives the average wavelength. In the same way, Figure 3b shows the function $E\,I(E)$ as a function of E so that the quotient of the areas under the curves of Figures 3b and 1b gives the average energy. We calculated these areas using the Calculus function of the Analytical tool available in the Microcal Origin 6.0 software package. The average wavelength and energy values obtained were $\langle\lambda\rangle$ = 670 nm and $\langle E\rangle$ = 2.14 eV, respectively. From this last value, we will obtain for $hc/\langle E\rangle$ the result 580 nm, which is different than $\langle\lambda\rangle$, as expected.

On the other hand, Figure 4 shows the function $(1/E)\,I(E)$ as a function of E. The quotient of the area under the curves of Figures 4 and 1b gives the average value $\langle 1/E\rangle$ = 0.540 $(eV)^{-1}$. Now, eq 5 leads to the right value of $\langle\lambda\rangle = hc\,\langle 1/E\rangle$ = 670 nm.

In conclusion, we demonstrated that for the blackbody radiance spectrum $\langle\lambda\rangle \neq hc/\langle E\rangle$ and $\lambda_{max} \neq hc/E_{max}$. Instead, $\langle\lambda\rangle = hc\langle 1/E\rangle$ and $\lambda_{max} = hc(1/E)_{max}$. These results are independent of the spectral intensity's shape, so they can be generalized for spectral distributions of any kind.

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Notes

The authors declare no competing financial interests.

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