Get the Basics Right: Jacobian Conversion of Wavelength and Energy Scales for Quantitative Analysis of Emission Spectra

Effective representation of data plays a vital role in scientific communication. Moreover, a different representation of the same raw data may facilitate better quantitative analysis. Often, signal data are recorded and presented as a function of the electromagnetic spectrum. Commonly, spectra are recorded in wavelength units, but presentation of data as a function of energy provides better physical insight. The inverse relationship between the two quantities presents some challenges and has sometimes led to incorrect conclusions, such as the assertion that the spectral response of the human eye is optimized to match the solar spectrum. Clearly, proper presentation of spectral data is critical for enlightening scientific investigation.

> Simply noting the intensity versus wavelength in photoluminescence spectroscopy is insufficient.

Photoluminescence (PL) spectroscopy is one of the most commonly used experimental methods in exploring photochemistry and photophysics. For *quantitative* analysis of the excited state of a system, PL intensity and spectral profile analysis is performed. In this case, simply noting the intensity versus wavelength is insufficient. For example, in the development of nanomaterials for luminescent devices, emission occurs over a broad range of wavelengths, with a single material often spanning a broad spectral window based upon multiple emissive sources. In such a situation, often found in semiconductor nanocrystals, two important subtleties arise in the PL spectra that must be properly addressed prior to quantitative analysis of the spectra.

Conversion of Signal Data from Wavelength to Energy Units. When multiple peaks are present in a spectrum, the units in which these peaks are plotted become important. Signal data recorded from a spectrometer in intervals of wavelength are often plotted in energy units, especially in materials science. Conversion of a value from wavelength to energy proceeds via the familiar

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

Thus, it may appear that mere conversion of abscissa values from wavelength to energy using the above formula is all that is necessary to produce a proper plot in energy units. Here, it is important to recall that signal values such as those recorded from a spectrometer are really *signal per unit wavelength* or *signal per unit energy*. Due to the inverse relationship between wavelength and energy, the intervals dλ in the wavelength spectrum are not evenly sized across the energy spectrum (Figure 1a).

If the recorded signal is considered some function $f(\lambda)$, then from conservation of energy

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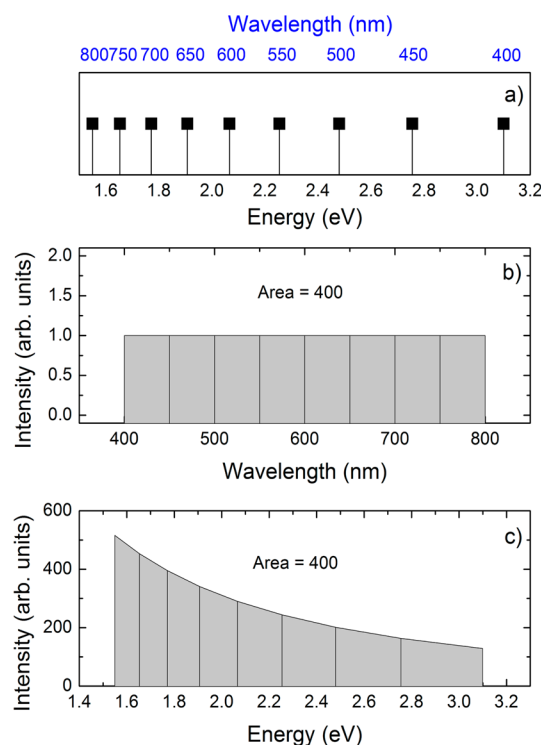

Figure 1. (a) Due to the inverse relationship between wavelength and energy, evenly spaced data intervals in wavelength are unevenly spaced in energy. (b) A constant signal of unity between 400 and 800 nm gives an area of 400. (c) The constant unity signal in wavelength, when properly converted to energy, gives a curve because the signal per unit energy is higher at lower energy/higher wavelength. The area of 400 is preserved, whereas if the signal had not been converted and of unity during conversion to an energy scale, the area under the curve would be incorrect.

Thus, combining eqs 1 and 2

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

The minus sign here can be ignored as it merely reflects the different directions of integration in wavelength and energy. Thus, to properly convert data recorded in units of wavelength, not only must the wavelength scale be converted using eq 1, but the signal values themselves must be scaled by (hc/E^2). This factor is called the Jacobian transformation.

To illustrate the effect, consider a constant signal of unity per nm between 400 and 800 nm (Figure 1b). The total (unitless) signal area over this range is 400. If this signal were improperly converted to energy units (eV) by application of eq 1 on the

abscissa without use of the Jacobian transformation for signal data, the apparent signal would be unity per unit eV over a range from 1.55 to 3.1 eV, resulting in a total unitless signal area of 1.55. Clearly, this result is incorrect. If instead the Jacobian transformation is applied, the signal values are no longer constant over the energy range, but the correct unitless signal area of 400 is obtained (Figure 1c).

The use of the Jacobian transformation on a normalized spectrum with a single peak, especially one with a narrow bandwidth, will have little effect. However, when multiple peaks are present in the spectrum, especially over a large energy range, the Jacobian transformation produces significant differences in the spectrum. The effect of this correction is demonstrated in Figure 2 for two limiting situations. In an

Figure 2. Corrected and uncorrected absorption (a) and fluorescence (b) spectra for CdSe nanocrystals (NCs) and fluorescence from a laser dye (c). The use of the Jacobian transformation is particularly important when multiple peaks are present in a spectrum. On the other hand, use of the Jacobian transformation on a broad peak changes the peak slightly without affecting the overall shape.

absorption spectrum (Figure 2a) or a broad-band emitter with multiple peaks such as a quantum dot with surface emission in addition to band edge excitonic PL (Figure 2b), the transformation significantly alters the spectrum. In contrast, a narrow-band emitter such as a laser dye (Figure 2c) or the band edge excitonic PL of a semiconductor nanocrystal is little affected by the transformation.

Populations and Line Shapes. While the Jacobian-corrected PL spectrum is now appropriate for quantitative analysis, further processing is required for extracting population information from relative peak areas. One may be interested in exploring whether different populations of emitters contribute to the presence of multiple PL peaks or very broad PL bandwidth. For population analysis and understanding of the origins of line width, one must further reduce the Jacobian-corrected intensity into a spectral line shape, $\sigma(E)$. The line shape contains the microscopic details of the emitter, Franck–Condon factors, and populations. It is dressed by the appropriate frequency prefactors to yield the observed intensities

$$I(\omega_I) = C\omega_I \int_{-\infty}^{\infty} e^{i\omega_I t} \langle \phi_i | \phi_i(t) \rangle \, dt \tag{4}$$

$$I(\omega_S) = C\omega_S^3 \int_{-\infty}^{\infty} e^{i\omega_S t} \langle \phi_i | \phi_i(t) \rangle \, dt \tag{5}$$

The subscripts I and S refer to the incident and scattered (emitted) photon; division by these prefactors to the appropriate power yields the line shape. As we have shown in recent works, in the analysis of nanocrystal spectra, correction for the Jacobian transformation in conjunction with this conversion to line shape provides the properly treated data for quantitative analysis and modeling of populations.

Figure 2 shows spectra of a broad-band absorber and emitter (CdSe semiconductor nanocrystal) and a narrow-band emitter (common visible laser dye). The absorption spectra of NCs are always broad. The NC PL spectra can be narrow or broad with two peaks based upon the surface thermodynamics of the system. We have specifically chosen a CdSe NC with broad-band PL spectra that highlights the need for these corrections.
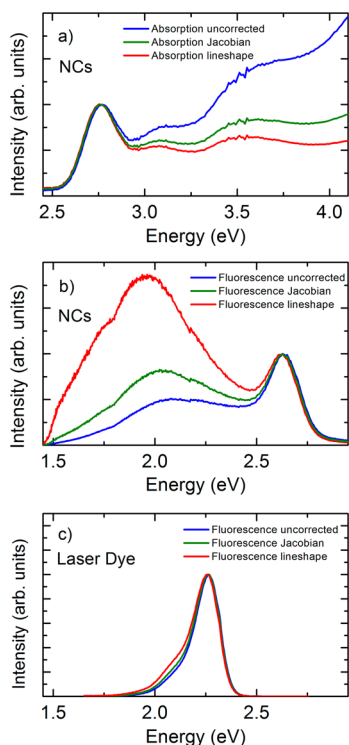
The absorption spectra of the NC (Figure 2a) clearly show the importance of correcting the raw data. While it is well-known that the absorption per unit wavelength increases at high energy, this additional analysis reveals that the transition probabilities are actually smaller for these high-energy transitions than those for the band edge exciton. The PL spectra of these NCs are shown in Figure 2b. Directly converting a spectrum from measured nm to eV yields an incorrectly processed spectrum that shows two peaks, with the lower-energy peak less intense. Incorporating the Jacobian correction makes the low-energy peak more pronounced. Should these peaks arise from different quantum states, one

may wish to relate their areas to populations. Doing so requires further conversion to line shape, with the assumption of a constant electronic transition moment integral for the two states. Performing this conversion reveals a marked increase in the relative area of the low-energy peak, the surface PL in the case of CdSe NCs. Finally, as a reference, the narrow-band system is represented by a simulation of a visible laser dye, Figure 2c. When the spectra are narrow, these effects are minor.

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■ ACKNOWLEDGMENTS

■ RELATED READINGS

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