

Wavelength considered harmful

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Wavelength units are still routinely used in some areas of spectroscopy. This is stupid, for reasons outlined below, and it almost always makes more sense to use direct energy units in places where you're not actually caring about the number of wave oscillations per unit length (looking at you, UV-Vis spectroscopists). Inertia is difficult to overcome, but they probably said that to Martin Luther as he nailed his ninety-five theses to the church door in Wittenberg.

I. INTRODUCTION

Spectroscopy, as a discipline, essentially boils down to interpreting graphs of how *something* responds to being irradiated by photons of different energies. These graphs consist of an x-axis that reflects the photon energy sent in, and a y-axis that shows how that *something* responded to said photon energy. These graphs can be interpreted to tell you a wide range of useful things, like 'what molecule have I made in my synthesis?', or 'what happened to my protein when I blasted it to pieces with an X-ray?'. This all sounds wildly familiar and comforting.

The whole gamut of possible spectroscopic measurements use photon energies that span well over ten orders of magnitude. It is therefore reasonable that different spectroscopists use different units to represent the kind of photon energies *they* tend to use in *their* measurements. In fact, what is normally the standard SI unit of energy, the **Joule**, is pretty annoying to use in spectroscopy as a Joule would be a massive amount of energy if it were carried by a single photon. Trying to give a single photon one Joule of energy is the spectroscopic equivalent of trying to squeeze Eric Pickles into a leotard: difficult, and someone is going to end up with an embarrassing radiation burn. Instead, we report photon energies in terms of other quantities that are directly proportional to the photon energy and give us a much more manageable number – frequency, wavenumber – or we use different units for the energy, like electronvolts. Sometimes we even report the ratio of the energy to a reference energy, or report the energy relative to another energy. All good, all easy.

However, some of us, and I am shamefully including myself in this bracket, opt to do something quite perverse. Shackled by historical convention, rather than report how our molecules respond to irradiation by plotting the response against energy (or something directly proportional to energy), we plot the response against something that is deliberately *inversely proportional* to energy. We use *wavelength* (λ) units to plot the spectra. Equation 1 shows the relationship between photon energy (E), optical frequency (ν), and wavelength (λ):

$$E = h\nu = \frac{hc}{\lambda} \quad (1)$$

So by plotting a spectrum against wavelength, we are really

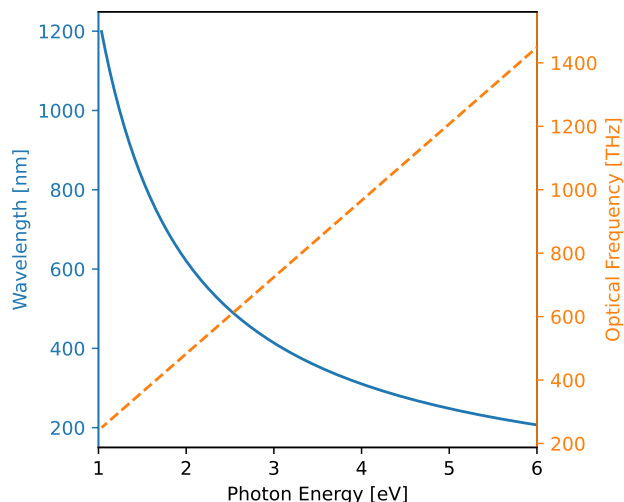


Figure 1: Wavelength (blue, solid line, left axis) and optical frequency (orange, dashed line, right axis) of various photon energies.

plotting it against inverse energy. This is problematic for several reasons.

II. THE PROBLEMS

A. The Scale Goes Backwards

Firstly, it's just plain *annoying* that the units aren't proportional to energy. The scale seemingly goes backwards (low wavelengths correspond to high energy and vice versa) so when you plot a spectrum against increasing wavelength the energy is actually decreasing from right to left, which flies in the face of the established Western cultural norm that things *increase* from right to left. This is annoying, but isn't the most annoying thing.

B. Non-Linearity of Units

If it was just that the scale was reversed, we could probably live with that and just remember to invert it in our heads when reading spectra. But that's not all. The most

annoying thing is that **the scale isn't linear**, as Figure 1 illustrates. A change in energy of 1 eV is a change in energy of 1 eV whether it's being added to 0.1 eV or 1000 eV. Table I shows what happens if we try and do the same thing with wavelength.

Wavelength (nm)	Photon Energy (eV)
500	2.48
510	2.43
200	6.20
210	5.90

Table I: Wavelength and photon energy.

A change in wavelength of 10 nm corresponds to a change in energy of 0.05 eV *if it is being added to 500 nm*. If it's being added to 200 nm, it corresponds to a change in energy of 0.3 eV – almost 10x more energy! This problem has a serious consequence because it makes it very difficult to quickly compare the linewidths ($\Delta\lambda$) of peaks in different regions of the EM spectrum. Differentiation of Equation 1 leads to a rough expression for the linewidth $\Delta\lambda$:

$$\Delta\lambda \propto \lambda_0^2 \Delta E \quad (2)$$

Where λ_0 is the wavelength at the centre of our peak, and ΔE is the linewidth in nice, normal, linear, energy space. Clearly, Equation 2 shows that we have to scale the wavelength linewidths by a factor of λ_0^2 if we want to compare the widths of peaks in wavelength space – and who has time to do that? The consequence of this is that stuff at the high energy (blue) end of our spectrum will get bunched up, and things at the low energy (red) end spread out, if we plot the spectrum as a function of wavelength. Again, this might be fine, but it means inferring things about the linewidth gets annoying – linewidth in frequency space is inversely proportional to state lifetime, but we can't easily make this comparison in wavelength space without always having to keep an eye on *where* the peak actually is - as Figure 2 shows.

An irritating consequence of this is that some spectra which are beautifully symmetrical in energy space look all stupid and bunched up on one side in wavelength space. Figure 3 shows exactly this: the same spectrum, in both energy (left panel) and wavelength (right panel) space. What a monstrosity! In energy space it's all symmetrical and lovely: the spectroscopic equivalent of the Taj Mahal. In wavelength space it is more like the 'Taj Mahal' Restaurant in a provincial English town: a one-star hygiene rating and terrible chutney-to-poppadom ratios. Furthermore, wavelength space gives more pixels to the low energy side of the spectrum and fewer to the high energy side, which seems unnecessarily discriminatory. Sure, it's not exactly Berlin 1933 or Apartheid-era Cape Town,

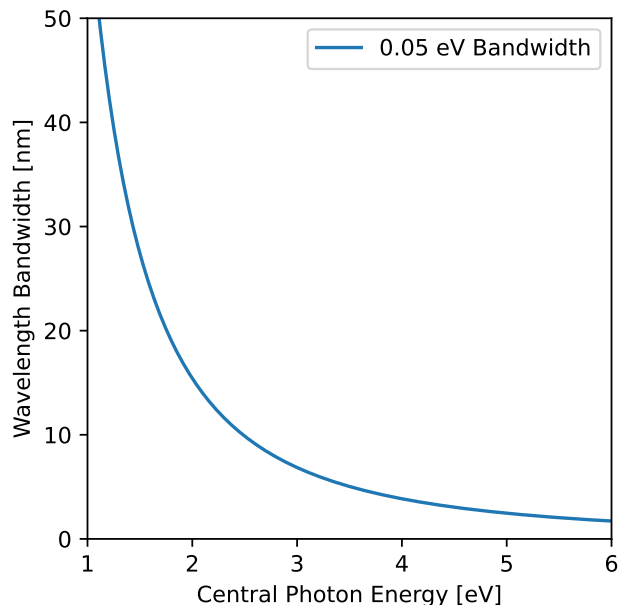


Figure 2: Wavelength-space bandwidth of a light source with an energy bandwidth of 0.05 eV as a function of central photon energy.

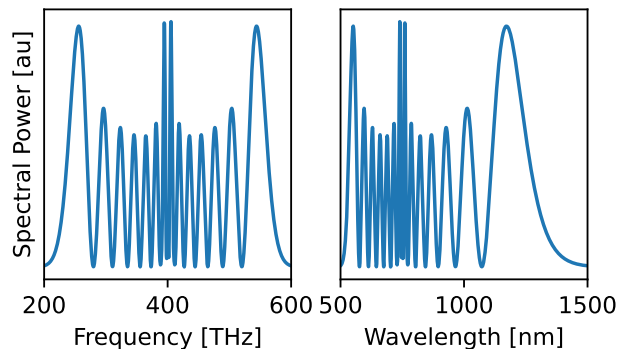


Figure 3: Spectrum of a laser pulse following self-phase modulation. Left: in frequency (energy) space. Right: in the equivalent wavelength space

but it might be a slippery slope. Why don't all energies deserve the same number of pixels in 2024? I can think of less useful EDI initiatives that exist.

C. Wavelengths are Subjective

If you've got this far, you probably haven't decided that all a load of subjective nonsense written by someone with too much time on their hands. But if you have, then here is a very non-subjective reason for not using wavelength as a measure of photon energy. **The wavelength of light**

depends on the medium it is travelling in. This can actually be seen in Equation 1 - the *optical frequency* is linked to the photon energy only by the Planck constant. The *wavelength* is linked to the photon energy by both the Planck constant *and* the speed of the light wave, c . c is not a constant, but depends on the refractive index, n of the material it is travelling through:

$$c = \frac{c_0}{n} \quad (3)$$

Where c_0 is the speed of the wave in vacuum. If our light wave enters a region with a different refractive index, the energy contained in the wave can't change (due to energy conservation), and therefore the frequency of the wave can't change. However, the refractive index has changed, and so the speed of the wave must change according to Equation 3. If the energy is constant and the speed changes, then by Equation 1, the wavelength must change to maintain the constant energy.

To illustrate this, imagine a visible light wave of optical frequency 500 THz travelling from air ($n = 1$) into water ($n = 1.33$), maybe it's entering a cuvette for some absorption spectroscopy. In the air, this light wave has a wavelength of 599.4 nm, but in the water, where it travels 1.33 times more slowly, the wavelength is 450.6 nm, a big change! When we detect the light wave back in air, we measure 599.4 nm again, but the *solution* experiences a different wavelength. I'm not the only person to have thought about this, and Rüdiger Paschotta over at RP Photonics writes about how small changes in the refractive index of air with temperature and humidity can have tangible and real effects on the wavelength accuracy of our measurements¹.

D. Light-Matter Interaction

Of course, the individual molecules in the solution described above are much smaller than a single wavelength, so they don't 'see' the wavelength of the light at all - all they sense is the oscillating electric field of the light, which oscillates at a fixed optical frequency. Light-matter interaction at this level is actually much more easily and intuitively explained using frequency than wavelength. Especially once spectroscopy becomes interesting and nonlinear, phenomenological explanations of things like sum- and difference-frequency generation are very difficult when we are used to thinking about wavelengths and not frequencies or energies.

Yet, in many educational settings, the wavelength picture

of light is taught first - which causes unnecessary confusion and complicates calculations. Anyone who has tried to explain spectroscopic unit conversions to a relatively inquisitive undergraduate will know that all of the aforementioned issues make it a bit of a nightmare for questions: '*why are small wavelengths big energies?*', '*why do we use these units then?*', '*hasn't anyone written a pointless paper about why it's stupid?*', and so on.

III. WHY USE WAVELENGTH?

Obviously there must have been a reason for the initial use of wavelength units. In fact, RP Photonics talks about the historical aspects of this in the aforementioned article. In the early days of optical physics, measuring wavelengths via interferometry and then calculating frequencies from the wave speed was the only way to analyse light. However, nowadays we can measure optical frequencies much more precisely than we can wavelengths - but the historical inertia in some parts of spectroscopy is hard to overcome. Other 'wave-y' fields, like radio and audio engineering, use frequencies instead of wavelengths for all the aforementioned reasons - and so do many spectroscopists, to be fair. It's mostly people doing UV-Vis that are still stuck in a time-warp.

So, is there any reason to still use wavelength units in spectroscopy? I would argue not really, except for a few cases like light scattering where the size of the object being analysed is of a similar scale to the wavelength and so interference effects become important. However, even in these fields, the analysis is complicated by the inclusion of all kinds of correction factors that deal with the fact that the wavelength changes when you move into different media - a lot of this could be avoided if energy units were used directly in the first place!

IV. THE SOLUTION

By now you probably agree that wavelength units are sometimes a bit irritating, but also probably don't think their use is a lingering relic from a bygone era that needs to be overturned, like hereditary peerages or statues of Confederate generals. You'd probably be right, but in a world where everything seems to be spiralling out of control, maybe arresting one silly piece of historical convention will lead to others, or at least make us feel a bit better.

Perhaps next time you do some UV-Vis spectroscopy or want to teach students about the colours of rainbow, you could do it in energy or frequency units. At least, some pedants will appreciate you.

¹ https://www.rp-photonics.com/spotlight_2021_04_30.html