SI3102 Photobiochemistry

LII: The World of Radiation

I. Light – what is it anyway? A pointlike elementary particle, like a bullet of energy (the photon)? Or is light better described as a travelling electromagnetic wave, a disturbance of the zero-field state of the empty vacuum, like a ripple on the sea?

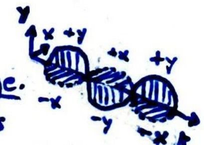
i. Light has features of both! Depending on the situation, it may be more useful to consider its particle-ness or wave-ness.

a. Individual photons interact with individual molecules (they are absorbed and emitted, raising and lowering the energy of the molecule respectively). Although it is easy to imagine what a wave that is half as intense looks like, this is where the particle-ness comes into play; a molecule with excess energy cannot get rid of it by emitting "half a blue photon". It is an all-or-nothing thing, and whole-number quantities of photons are exchanged in all interactions of light with matter.

α. Each photon carries an energy $E=h\nu$ where h is Planck's constant (6.626×10^{-34} Joule-seconds) and ν is the frequency in Hertz (or complete cycles per second).

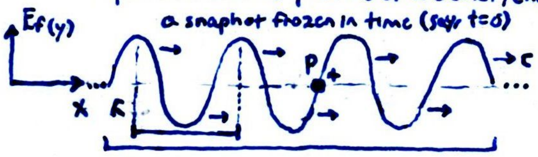
β. What does ν mean and what does it have to do with the "wavelength," λ?

A swarm of photons <u>acts like</u> a smooth wave of light (which is electromagnetic radiation), <u>on average</u>. And all light sources you are familiar with spit out trillions of trillions of photons, meaning their individuality is not easy to see for yourself.



There is also a magnetic field of the same shape, but pointing in and out of the page.

A pure stream of photons of one color/energy/frequency/wavelength ends up looking something like this:



Ef is the strength of the electric field at some place in the x direction. For this example it points in the y direction. Charged objects feel force when an electric field is present, and the field is defined to be a positive field in the y direction when it accelerates a ⊕ charge toward positive y.

This whole waveform (which continues on past my drawing) glides along the x axis at the speed of light c ($\sim3\times10^{8}$ m/s). λ is the distance at which features of the wave (peaks and valleys) repeat themselves. The wave travels <u>λ per cycle.</u>

Q: Examining the point P on the x-axis: what if a + charged blob with some mass was sitting there? What would it do?

A: It would shake back and forth at exactly the frequency ν, responding to the force like a kid being pushed back and forth on a swing. ν is then the number of complete cycles of motion and the number of cycles of light wave oscillation that pass per second, and as a result, <u>$c=\lambda\nu$</u>. So the energy of a single photon can also be interpreted in the wave picture, through λ.

ii. Just as a macroscopic object like a metal ball responds to an oscillating electric field by starting to shake, quantum systems like molecules (themselves consisting of charge-carrying nuclei and electrons) respond to light, but can only do so by moving between <u>distinct energy levels</u>. Level structure is arguably a signature of quantumness in general.

iii. The gap crossed between two energy levels by absorbing or emitting a photon is the energy of the corresponding photon, and photons that are mismatched to these energy differences <u>do not</u> effect transitions between quantum states. In effect, shooting photons at a sample/shining light on it and measuring absorbance, emission, fluorescence etc. directly probes the quantum structure of matter, including its electron orbitals, which are responsible for its bonding and reactivity.

a. This is an entire discipline of chemistry called <u>spectroscopy</u>, which is largely responsible for our understanding of how molecules are put together.

b. The absorption of visible-frequency photons is responsible for our entire perception of color. And, as will be shown, there is an entire universe of "colors" beyond ROYGBIV, ranging from ultra-low frequency radio waves to lethal gamma radiation.

c. Photochemistry is the deliberate use of photons, usually visible or ultraviolet (relatively high energy), to trigger movements of electrons between orbitals, leading to the breaking or the formation of bonds.

α. Photochemistry, quantum chemistry and spectroscopy are joined at the deepest level.

d. For a system to respond to light, as in the case of a macroscopic object, the transition has to somehow <u>redistribute charge</u> or tilt a magnetic part of the system (via the magnetic field component of light)...

2. For every kind of light on the electromagnetic spectrum, there is an associated kind of physical process, a kind of internal structure, an energy scale, and a characteristic time/frequency for processes to take place. (KEY TAKEAWAY: L2)

hard (high energy) X rays sometimes lumped in with γ

radio waves | microwaves | (IR) infrared | visible | (UV) ultraviolet | X-rays | gamma (γ) radiation

extreme low-frequency radio $\lambda \approx 5000$ km $\nu \approx 60$ Hz used by military to communicate with submarines through km of seawater, bends around mountains

Shortwave (ham) radio $\lambda \approx 10$ m $\nu \approx 30$ MHz, reflects off upper atmosphere plasma (M = mega, 10^6)

your microwave oven $\nu \approx 2.4$ GHz or 2450 MHz

"X band": used for radar, EPR, satellite comms. $\nu \approx 10$ GHz

for infrared $\lambda \approx 1$ mm $\nu \approx 300$ GHz soft "collective" vibrations of liquids

mid-IR $\lambda \approx 5$ μm typical molecular vibration

near IR $\lambda \approx 1100$ nm multi-vibration excitation

red $\lambda \approx 400$ nm

both visible and ultraviolet (together called UV-vis) are high enough energy to do photochemistry

blue-violet $\lambda \approx 400$ nm

UV-C $\lambda \approx 200$ nm kills cells

vacuum/extreme ultraviolet $\lambda \approx 10$ nm used to burn silicon into processors

soft X-ray $\lambda \approx 2$ nm for photoelectron spectroscopy and crystallography

hard X-ray $\lambda \approx 0.1$ nm medical/security imaging passes through matter

$S=\frac{3}{2}$ $S=\frac{1}{2}$ $^{57}Fe^* \rightarrow {}^{57}Fe$ emission

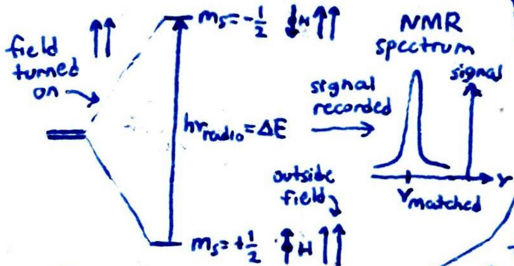
Crab Nebula emission $E \approx 450 \times 10^{12}$ eV = 450 TeV electrons moving near the speed of light inside pulsars $\lambda \approx 1.35$ am $= 1.35 \times 10^{-18}$ m Kinetic energy of 450 flying mosquitoes put together

low energy, low ν, high λ, slow events ⟵ ⟶ high energy, high ν, low λ, fast events

Used for NMR (nuclear magnetic resonance) $\nu \approx 300$-600 MHz

Like electrons, nuclei have spin and act like bar magnets.

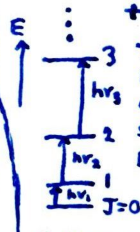
Placing a H nucleus in a molecule in a magnetic field causes different orientations of its magnet to have different energies (based on whether it aligns favorably with or against the outside field).



Radio photons flip the orientation of the spin, and watching the nucleus pass into this excited state says something about how the nucleus is connected to its neighbors, which have their own local magnetic spins that the H nucleus can feel, leading to very complex level structures. Decoding them can determine how a molecule is assembled.

Microwave photon energies are matched to two kinds of processes: making polar molecules rotate and reorienting electron spin (electron paramagnetic resonance, kind of like NMR).

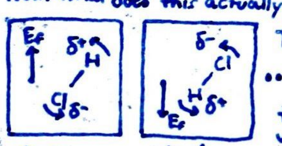
Consider $\overset{\delta+}{H}$–$\overset{\delta-}{Cl}$ ⟶ dipole



The molecule is fixed to spin only at certain speeds, labeled by the angular momentum number J.

So there is a whole hierarchy of rotational states, a ladder, and single photons carry out excitation ($\Delta J = +1$) or are emitted to slow the rotation of the molecule ($\Delta J = -1$). Because these energies depend on the rotational inertia of the molecule, they can be used to calculate H-Cl's bond length if the masses of the nuclei are known.

Now, what does this actually look like?



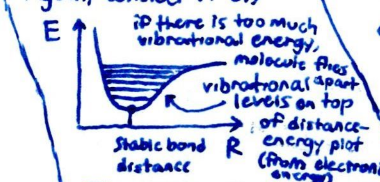
t = 0 $t = \frac{1}{2\nu}$

... The molecule is torqued/spun faster as it tries to align with the electric field!

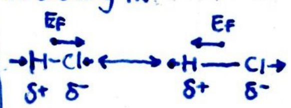
Microwaves cook food by doing this to H_2O, which spins faster and bangs into other molecules, heating them up.

Similarly to rotations, there is also an energy hierarchy of molecular vibrations. The stiffer the bonds involved and the lighter the nuclei, the higher the frequency of the vibration.

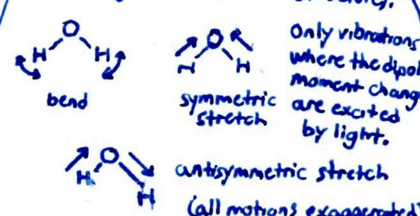
Again, consider H-Cl,



The electric field of light interacts with the dipole of H-Cl, squashing and stretching it.



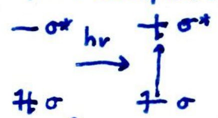
More complicated molecules have many kinds of coexisting vibrations, which can be used to fingerprint them (or fragments of their structure).



Only vibrations where the dipole moment changes are excited by light.

These photons induce color (when molecules absorb red and reflect blue, they look blue to us) and trigger genuine photochemistry.

The simplest example is H_2.

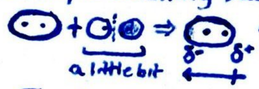


σ^2 configuration ⟶ $\sigma\sigma^*$ configuration

$(X\,^1\Sigma_g^+) \longrightarrow (B\,^1\Sigma_u^+)$

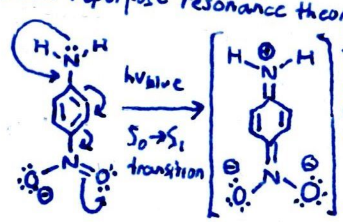
The bond is dramatically weakened! This is termed the "Lyman band" by astronomers and is $\lambda \approx 100$ nm – very high energy. What is happening to the electron density?

 is being partially mixed with  by the field – the electron density is sloshing back and forth as the transition proceeds



and likewise in the other direction, with oscillating polarization of the whole molecule

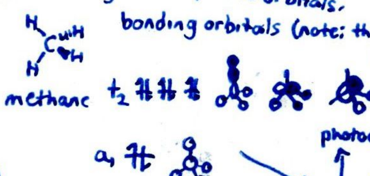
The UV-visible spectrum of para-nitroaniline is basically dominated by one feature. A detailed quantum model will be difficult to build by hand, but we can repurpose resonance theory.



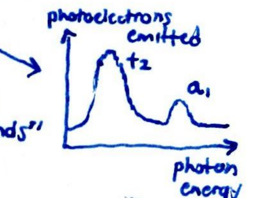
The excited state, produced by swinging electronic charge between orbitals, qualitatively resembles this minor resonance form of the ground state molecule.

$S_0 \rightarrow S_1$ λ peaks broad from 350-400 nm, uv/blue absorbed → compound is yellow-orange

Rips out tightly held core electrons from matter, sending them flying away to the vacuum. This is useful for probing A. elemental percentage composition of materials and B. finding experimental proof of MO theory by ionizing from specific orbitals.



hard to explain with "4 equivalent sp^3 bonds"



corresponds to excited states of the internal structure of the protons+neutrons in a nucleus; used to do Mossbauer spectroscopy (rare and specialized technique for iron and some other metals)