Warning: May contain chemistry…

And cats.

And drawings which demonstrate that I should not give up my day job to become an illustrator

Pigments and Colors and Dyes, Oh My!

Some of the chemistry behind the colors we see.

Mike Shaw

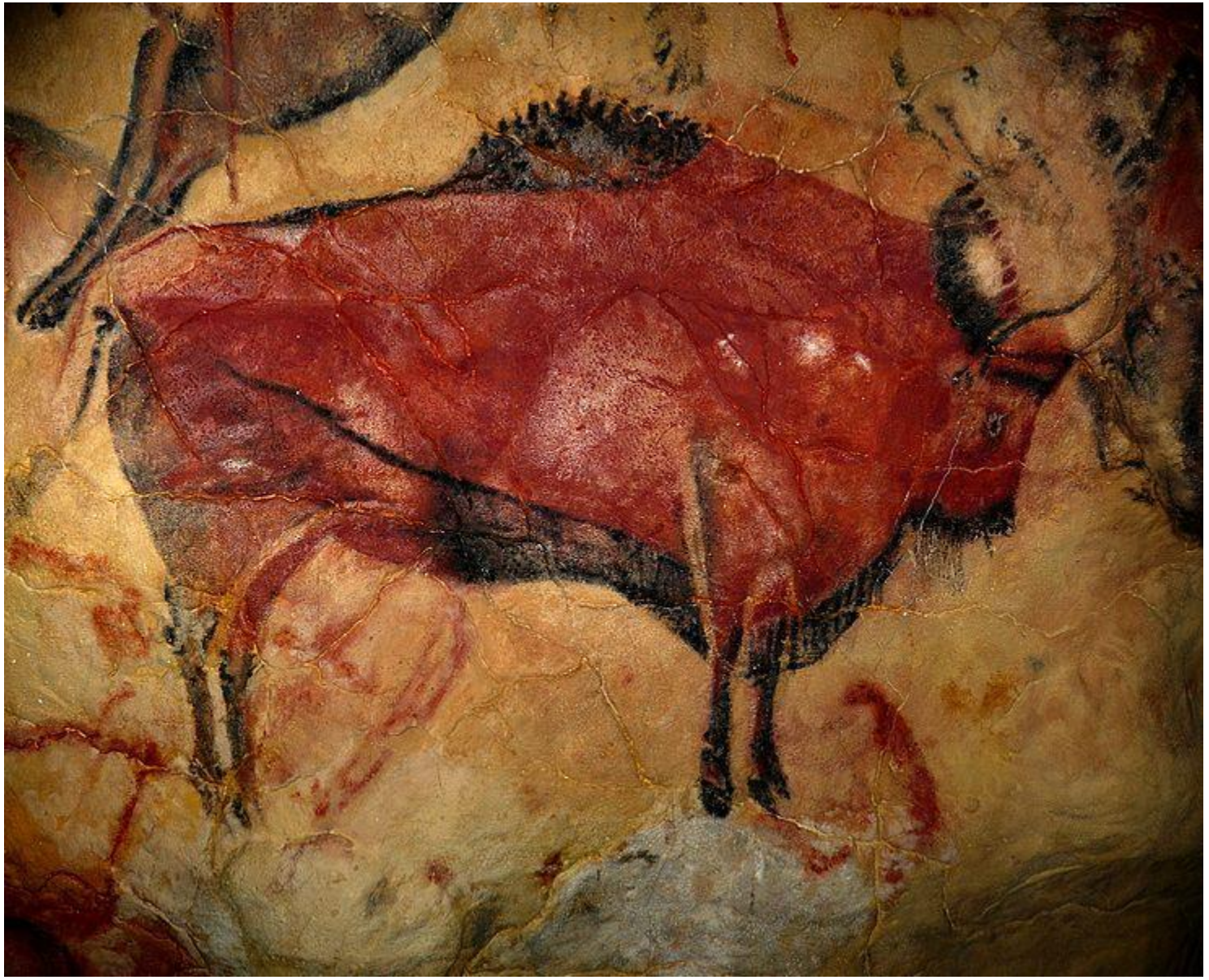
Science Circle

Feb 16, 2019

Humans like art.

- Bison drawn in red ochre, Altamira caves in Spain
- 16,500 to 15,000 BCE

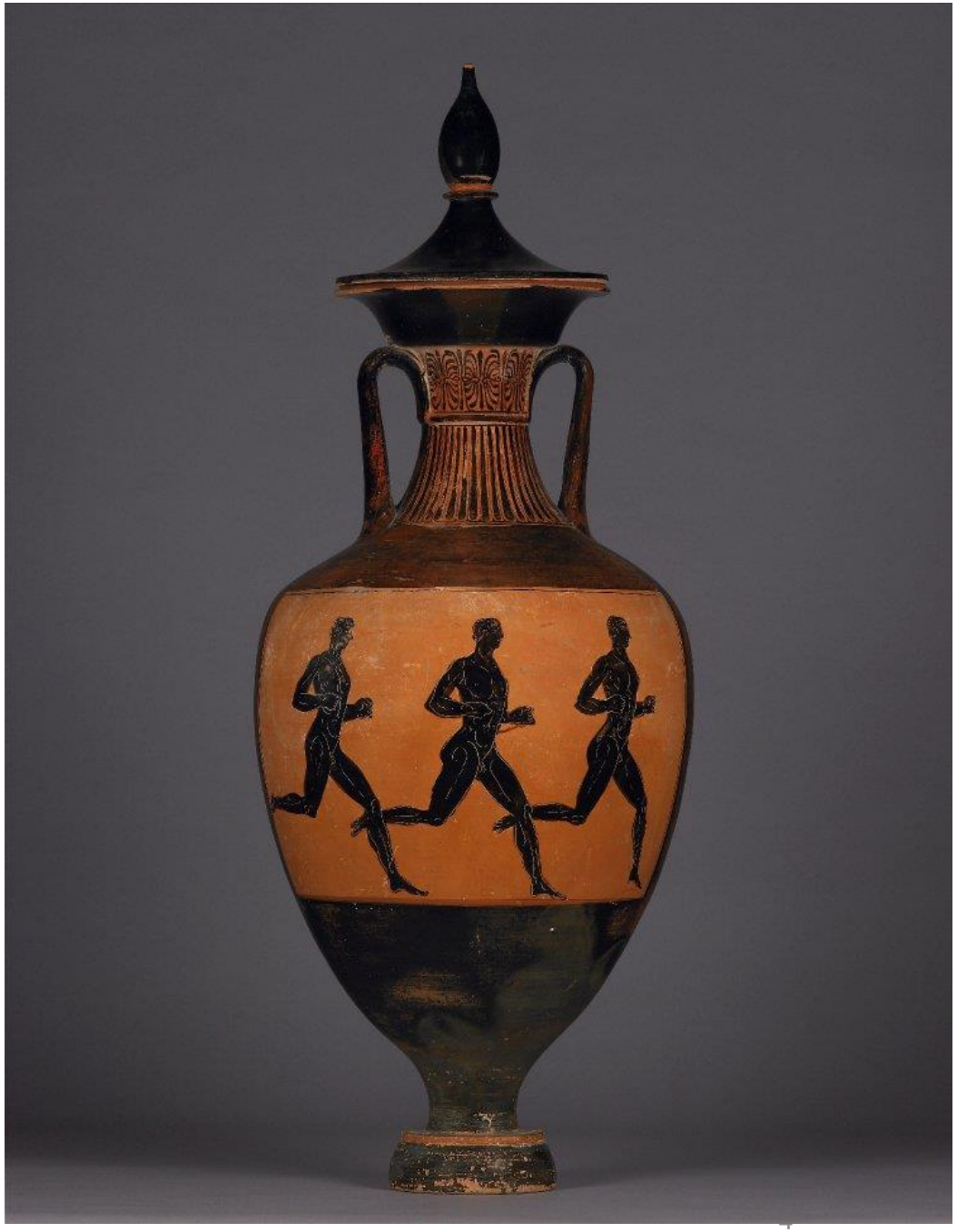
- Red ochre is hematite, Fe_2O_3



Public domain image from https://en.wikipedia.org/wiki/File:AltamiraBison.jpg

Black Figure Vase, ca 333 BCE

- Make a clay pot
- “Paint” the figures on it with a slip: dilute clay with larger particle size
  - scratch details in
- Fire at 800°C
  - Make red Fe_2O_3
- Fire at 950°C with green wood
  - Make CO, then black Fe_3O_4… almost smelting
- Allow air back in, cool down kiln
  - Slip is now glass: protects black figure while rest of pot turns red again



prize/trophy / Panathenaic amphora, , object 1856,1001.1, The British Museum
Image 1 of 26
https://www.britishmuseum.org/research/collection_online/collection_object_details.aspx?objectId=398787&partId=1&museumno=1856,1001.1&page=1

The Siren Vase: Red Figure Pottery

- 480-470 BCE
- More advanced technique, same 3-stage firing process, different slips and incision of patterns used.
- Hematite vs. magnetite

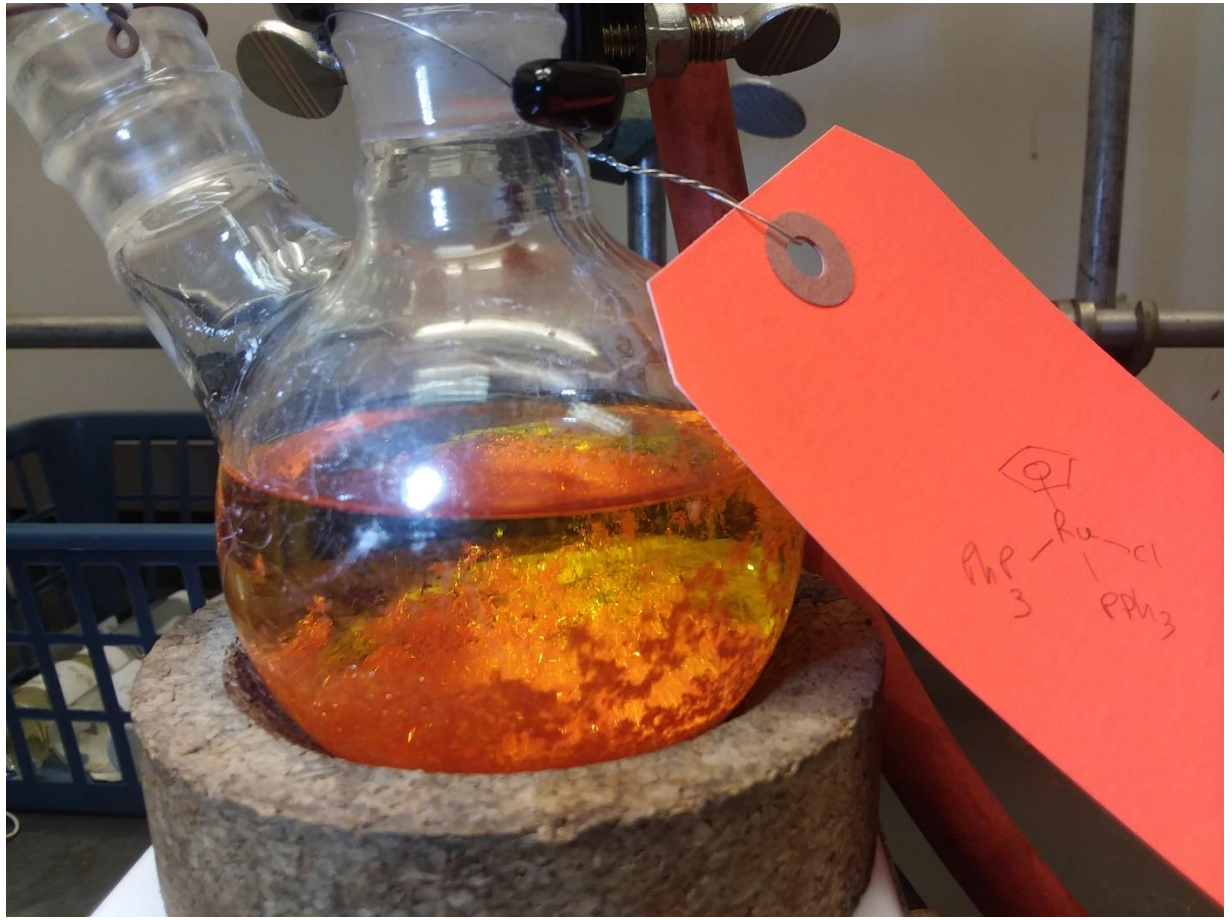
The Siren Vase, object # 1843,1103.31, The British Museum
Image 6 of 8
https://www.britishmuseum.org/research/collection_online/collection_object_details/collection_image_gallery.aspx?partid=1&assetid=478976001&objectid=399666

Pigment vs Dye?

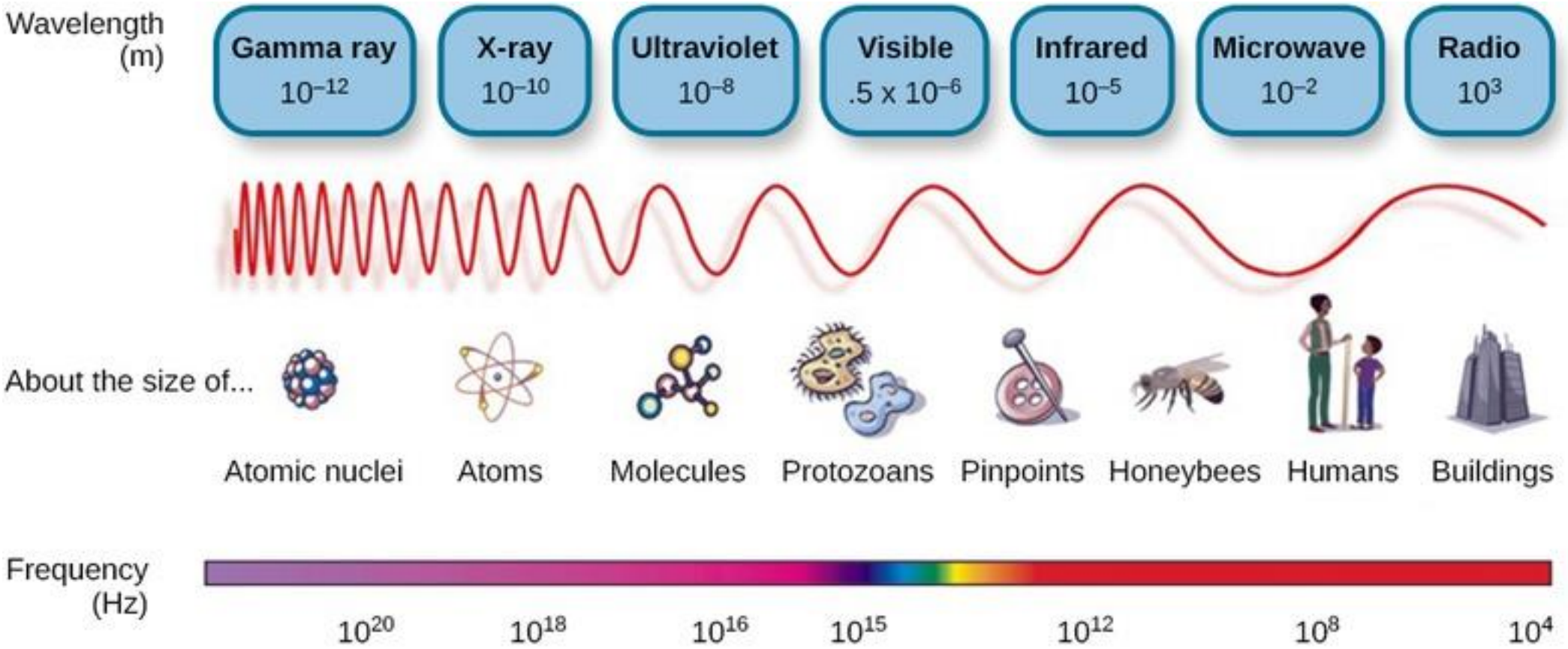
- The difference is solubility
- Pigments are generally insoluble
- Dyes are generally soluble, but need to be anchored to whatever is being dyed either naturally, or through the use of additives (mordants)

“Pigments from the Renaissance”… (SLAM 2003)

Orange Speedbump

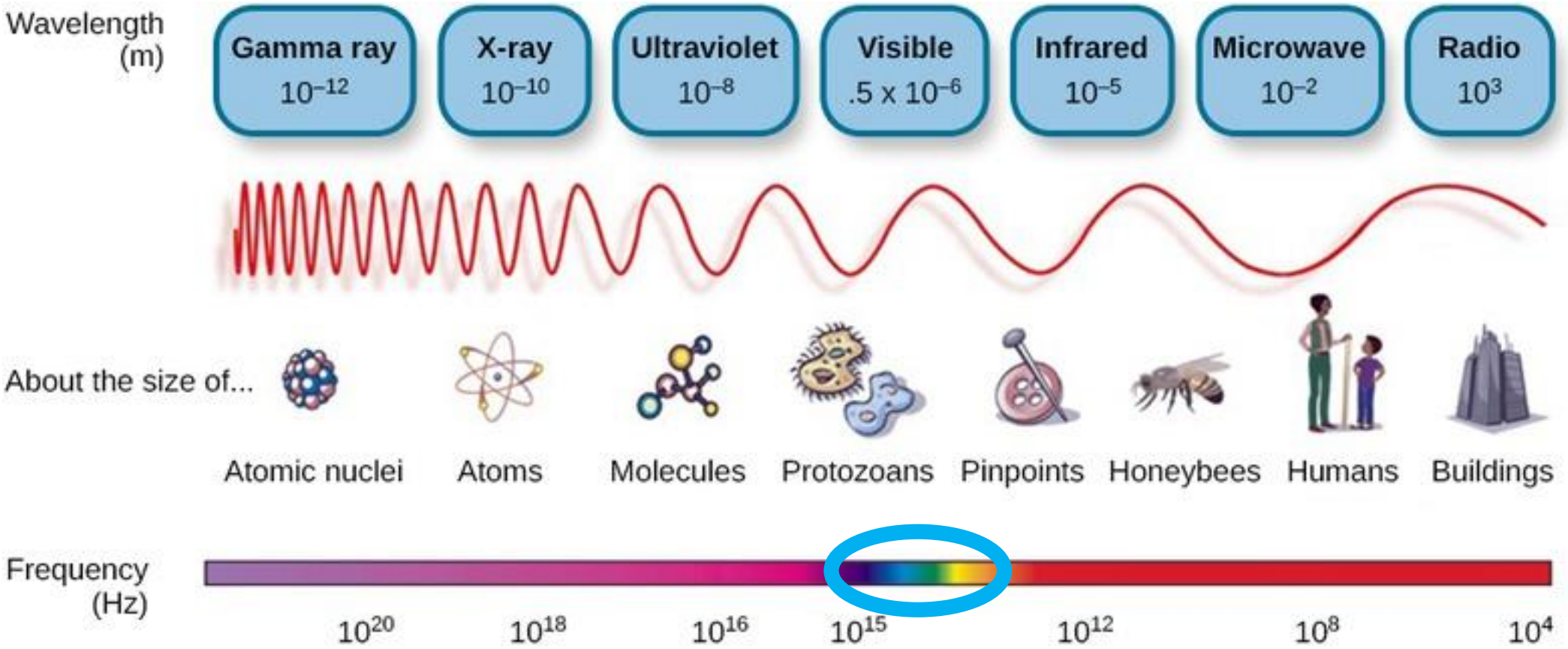


Light is just one form of electromagnetic radiation…photons.



https://www.oercommons.org/courseware/module/15318/overview

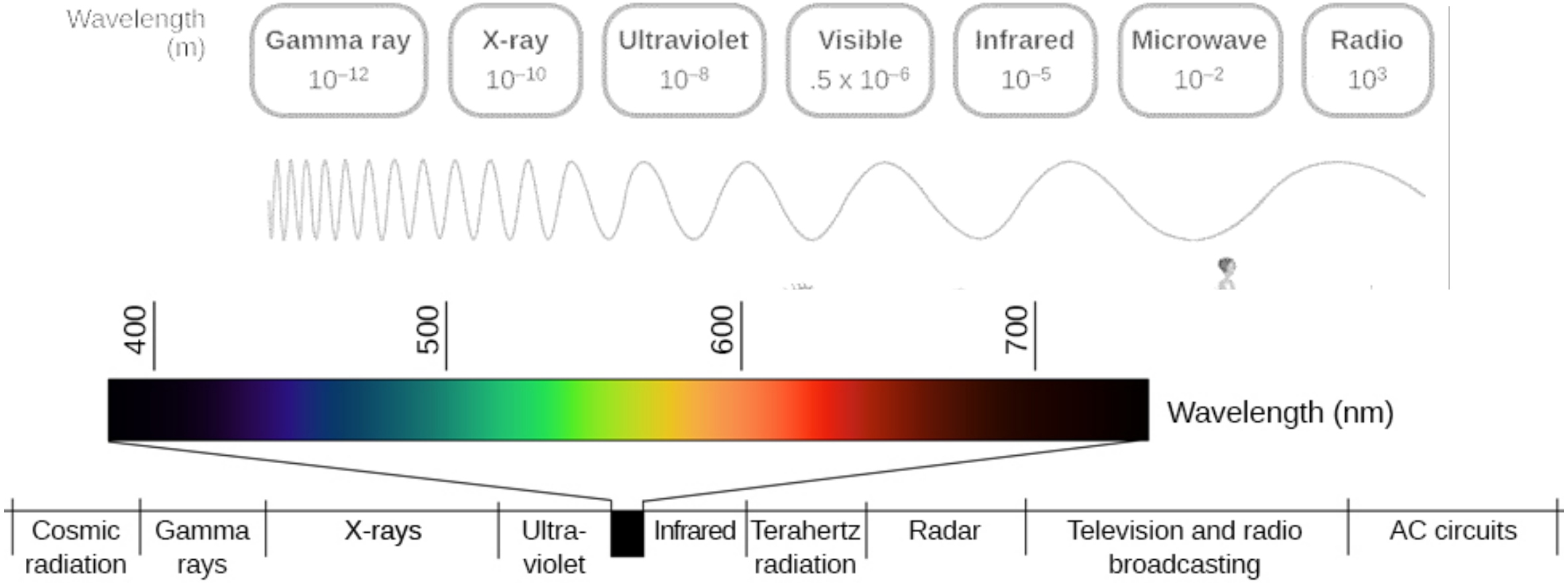
Light is just one form of electromagnetic radiation…photons.



What we see!

https://www.oercommons.org/courseware/module/15318/overview

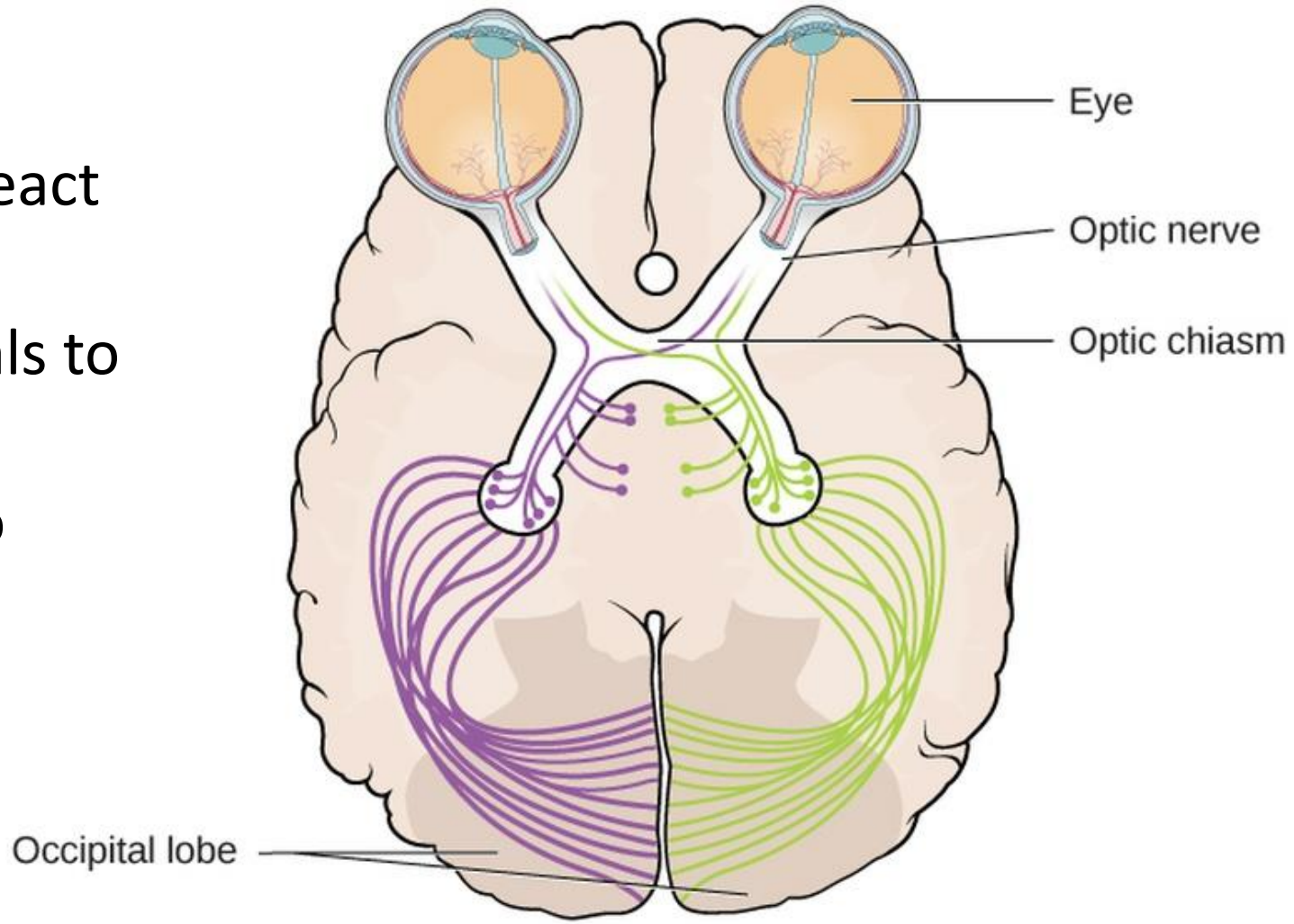
Light is just one form of electromagnetic radiation…photons.



https://www.oercommons.org/courseware/module/15318/overview

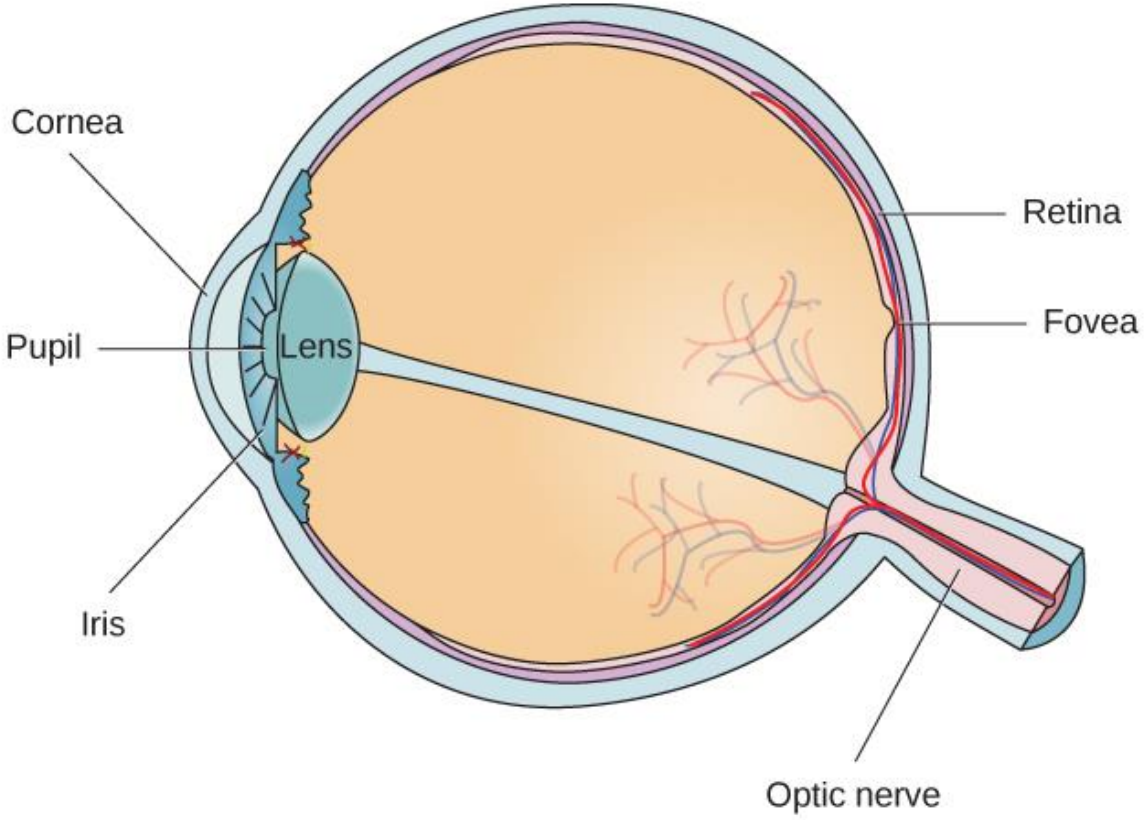
Perception of color is constructed within your brain!

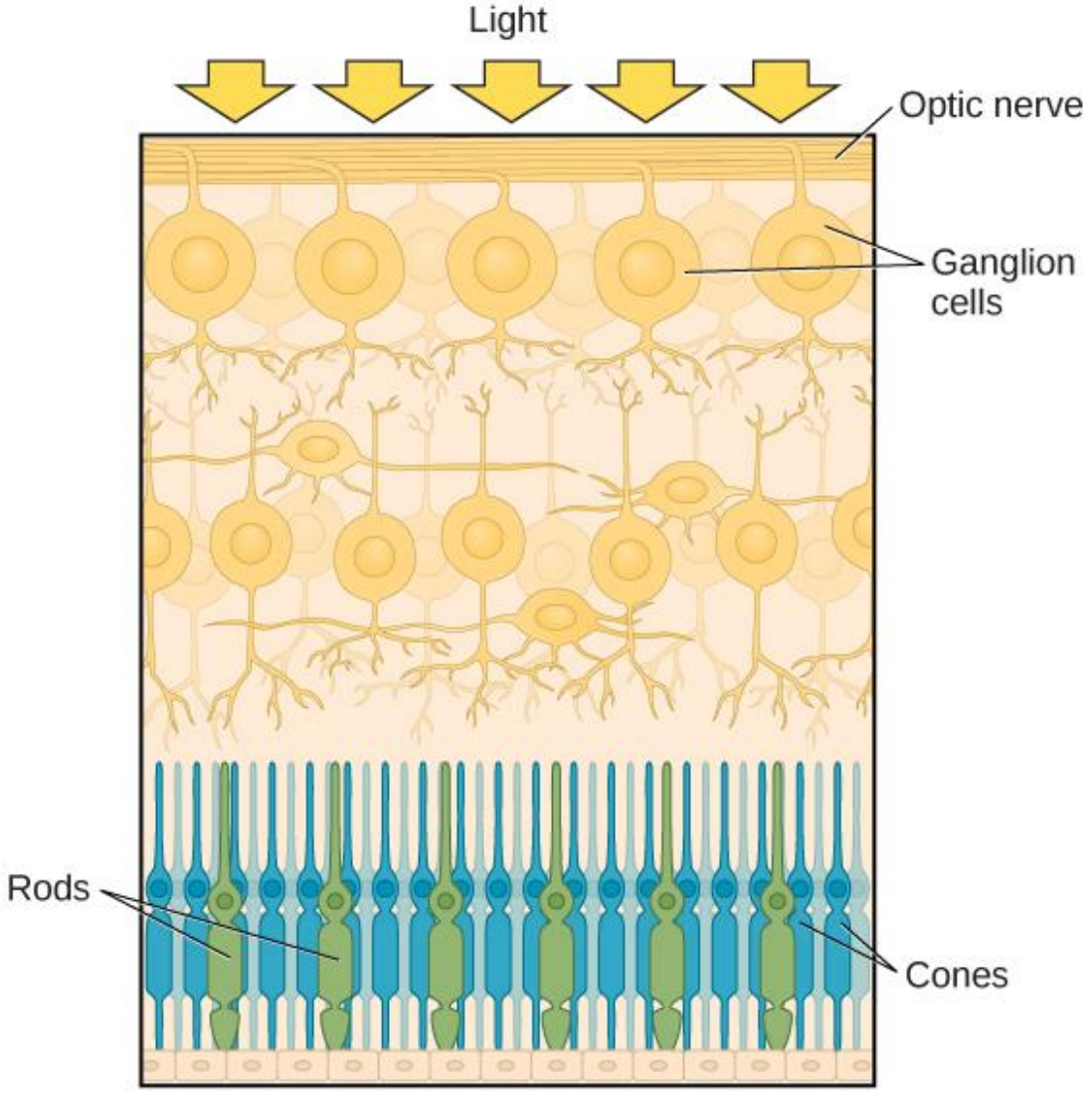
- Eyes focus image on retina
- Specialized cells in retina react to light
- Specialized cells send signals to nerve cells
- Nerve cells transmit info to brain
- Brain processes image into perception.



https://www.oercommons.org/courseware/module/15319/overview

Perception of color is constructed within your brain!





https://www.oercommons.org/courseware/module/15319/overview

Playing with your brain… (bwa ha ha)

Don’t read the words.

Name the colors out loud

RED

ORANGE

YELLOW

GREEN

BLUE

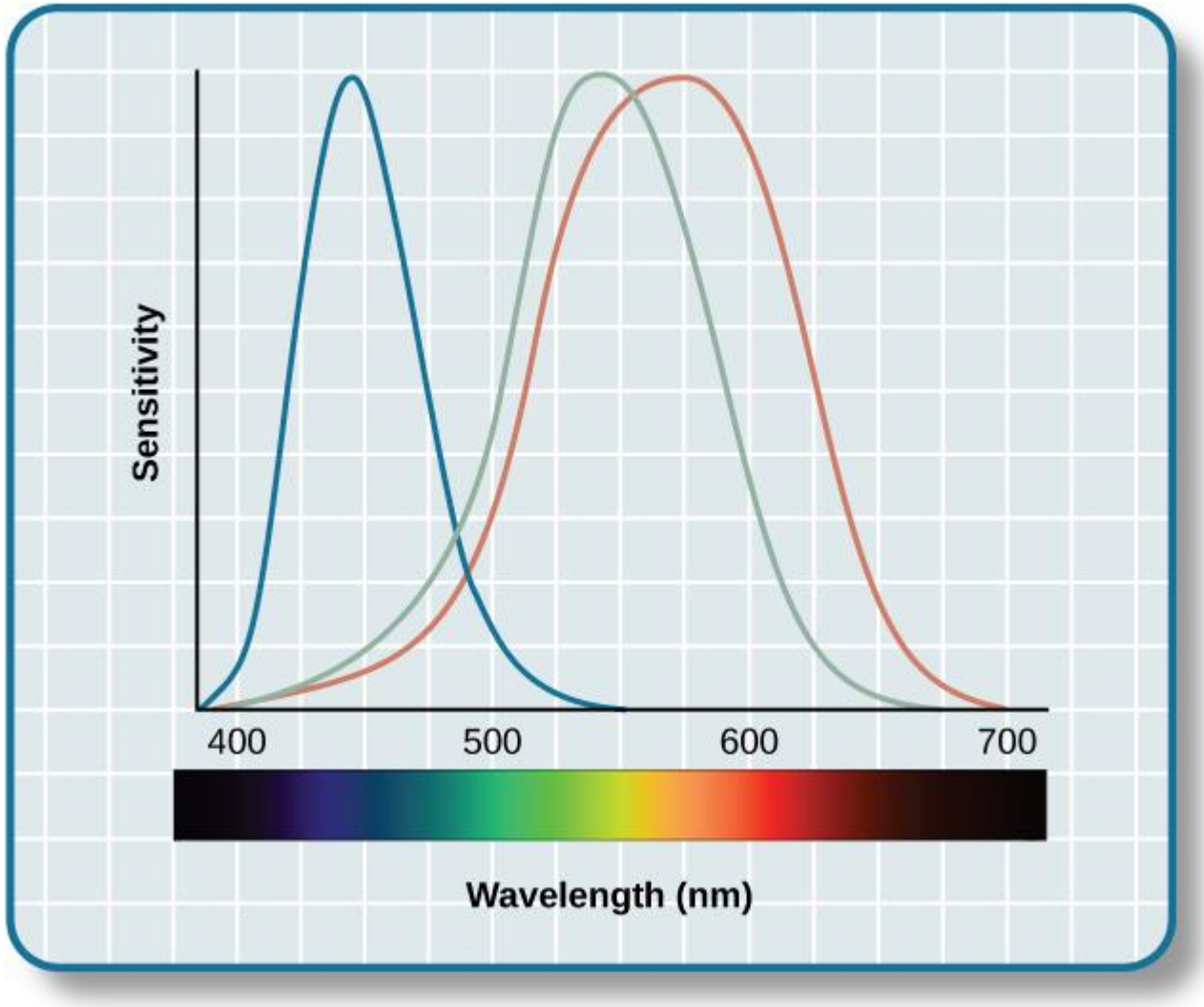
PINK

BROWN

But keep your microphone off please…

Perception of color is constructed within your brain!

- Rods are sensitive to light, but give little wavelength information
- 3 types of cones, each sensitive to a different wavelength profile
- There are several theories about how brain assembles this info into perception of color



https://www.oercommons.org/courseware/module/15319/overview

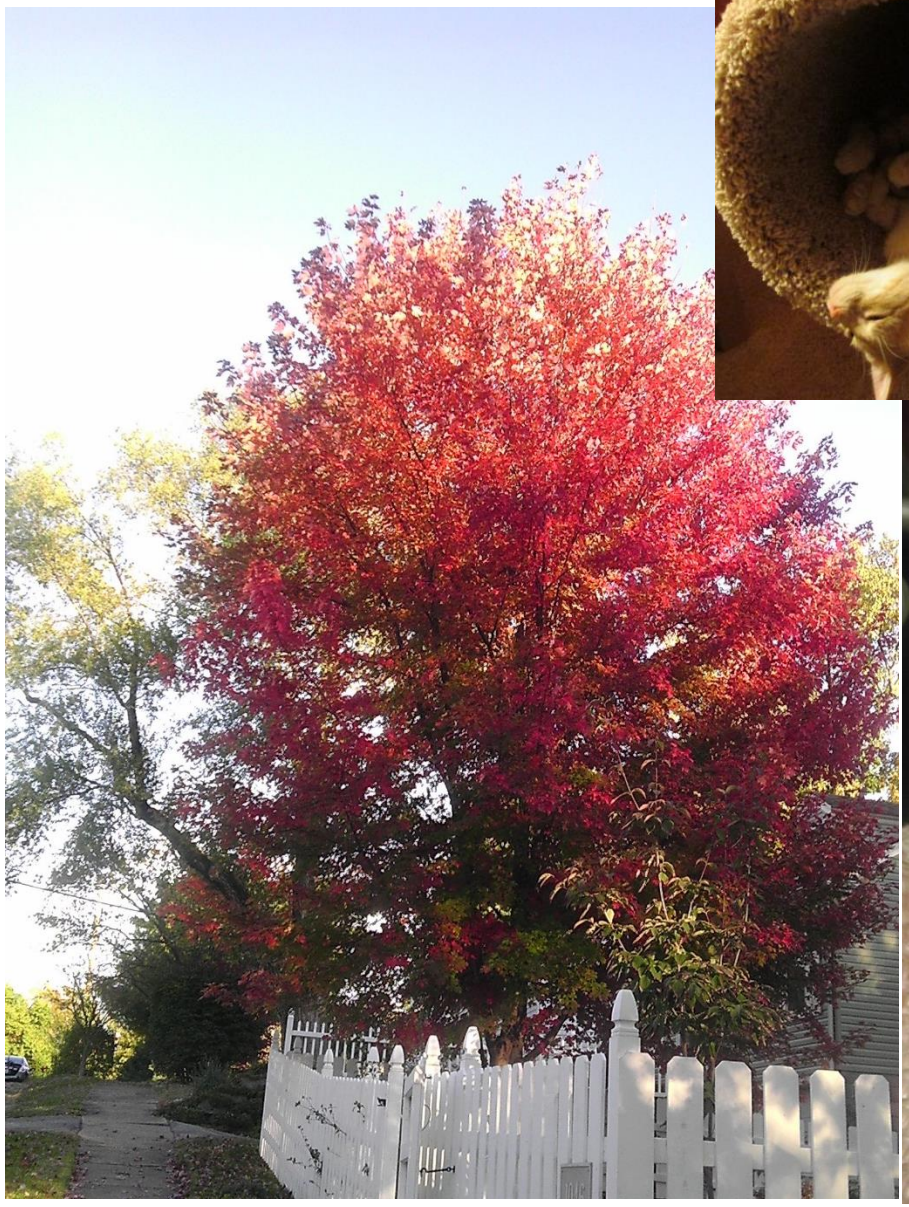
Attributions for Psychology section…

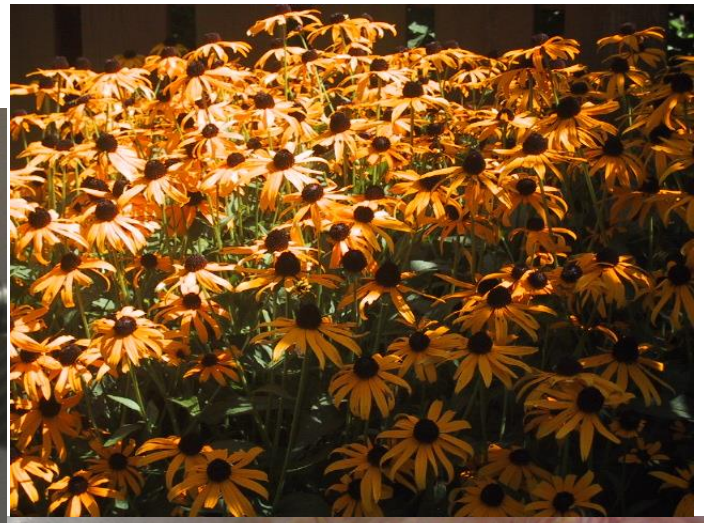
- Authors: Rose M. Spielman, Kathryn Dumper, William Jenkins, Arlene Lacombe, Marylyn Lovett, Marion Perlmutter

- Psychology course at OERCommons.org provided by Rice University
  - https://www.oercommons.org/courseware/8430

- Shared under Creative Commons Attribution 4.0

Orange Speed Bump



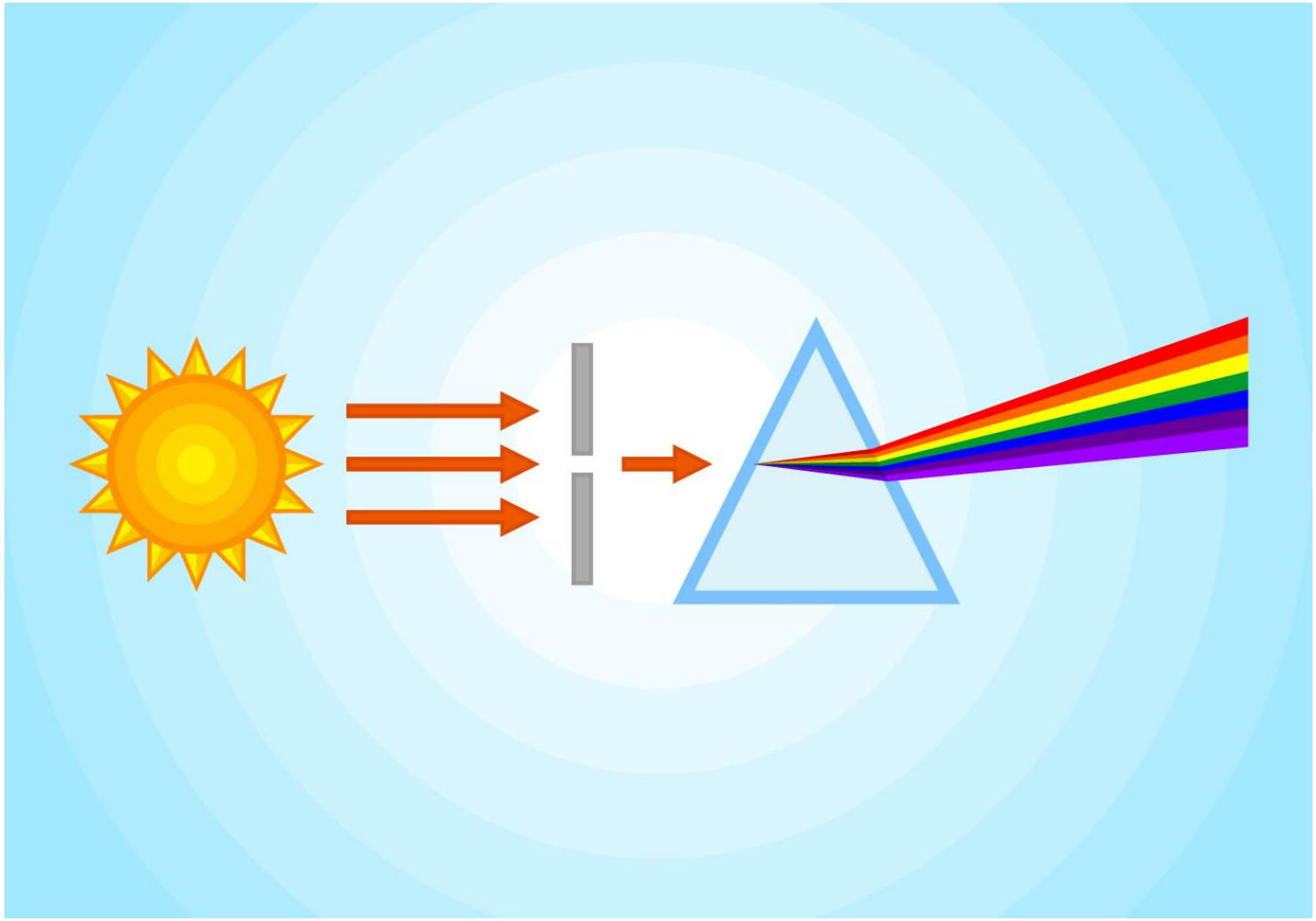


How we get colours….

- Dispersion
  - Prisms, dispersion gratings, scattering
- Interference
  - A nice video of soap film, by Paul Doherty at the Exploratorium https://www.exploratorium.edu/snacks/soap-film-on-can?media=7399
  - The explanation is here: https://www.exploratorium.edu/snacks/soap-film-interference?media=7448
- Absorption
  - Property of substances

Dispersion

- Refraction
- Butterfly wing
- Colloidal solutions



Vector illustration credit:
https://www.vecteezy.com/vector-art/184541-outstanding-prism-vectors

Lycurgus cup

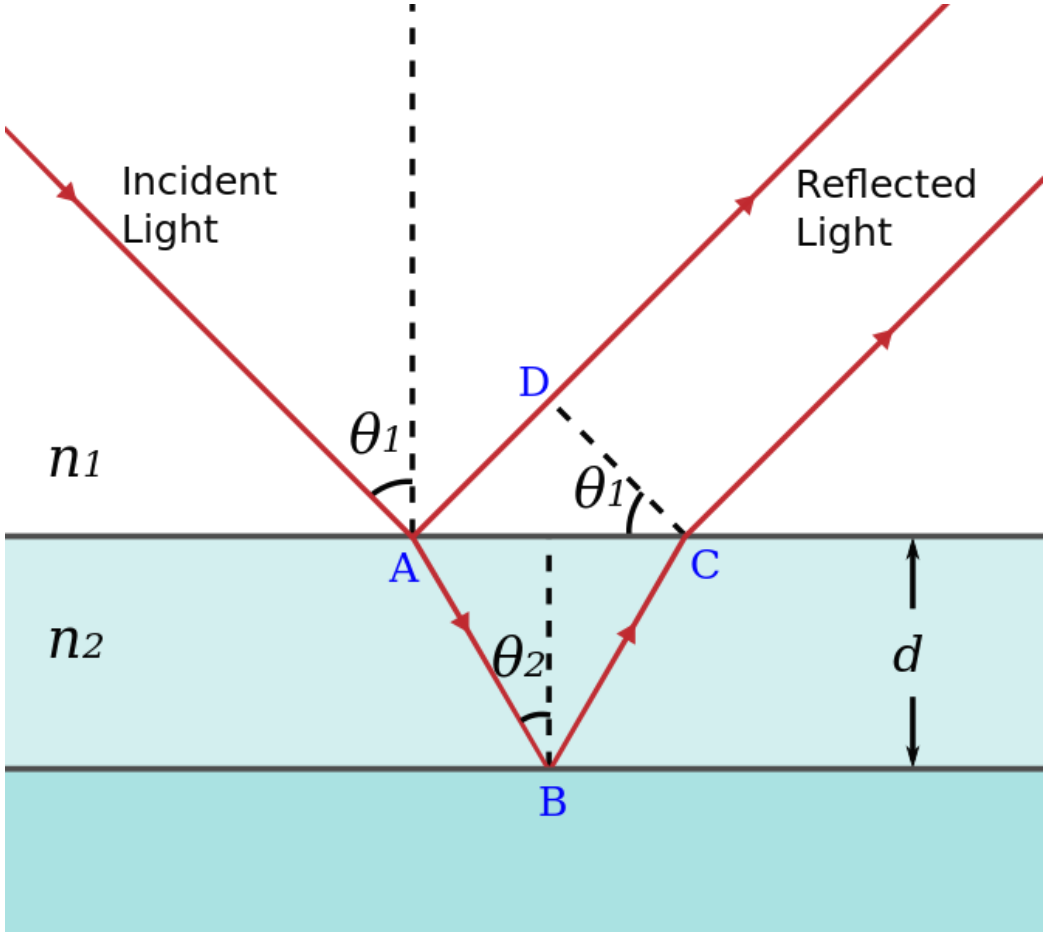
- Images from British Museum site
- Difference in color due to scattering off of gold and silver nanoparticles.
- 4th Century

Left: Image 1 of 42, Right, Image 6 of 42.
https://www.britishmuseum.org/research/collection_online/collection_object_details/collection_image_gallery.aspx?partid=1&assetid=63061001&objectid=61219

Reflected light

Transmitted light

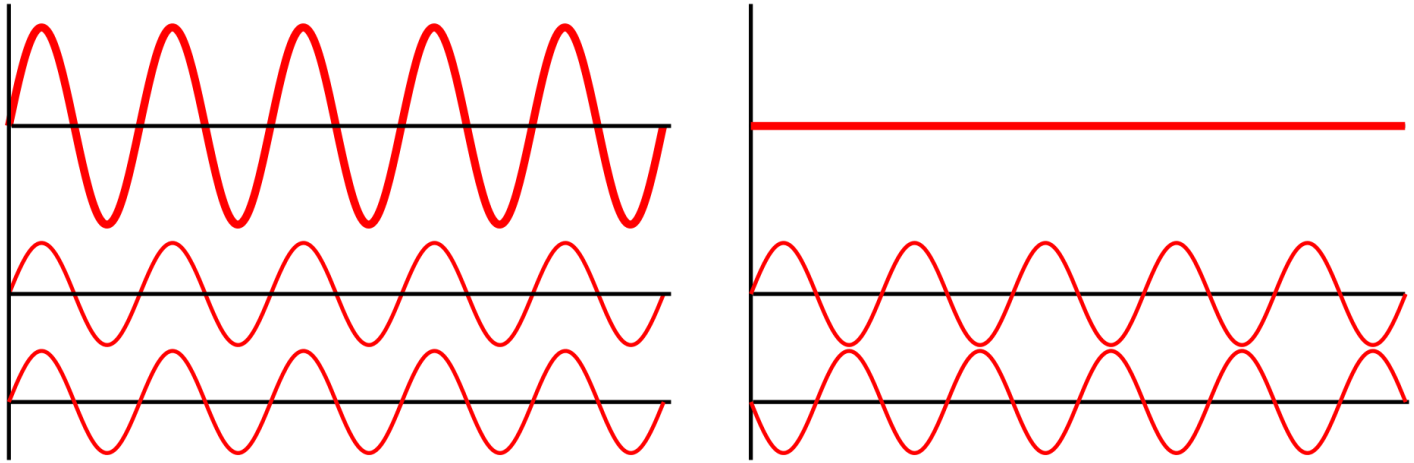
Interference



File:Thin film interference.svg. By original version: Nicoguaro - Own work.
https://commons.wikimedia.org/wiki/File:Thin_film_interference.svg

Constructive Interference

Destructive Interference

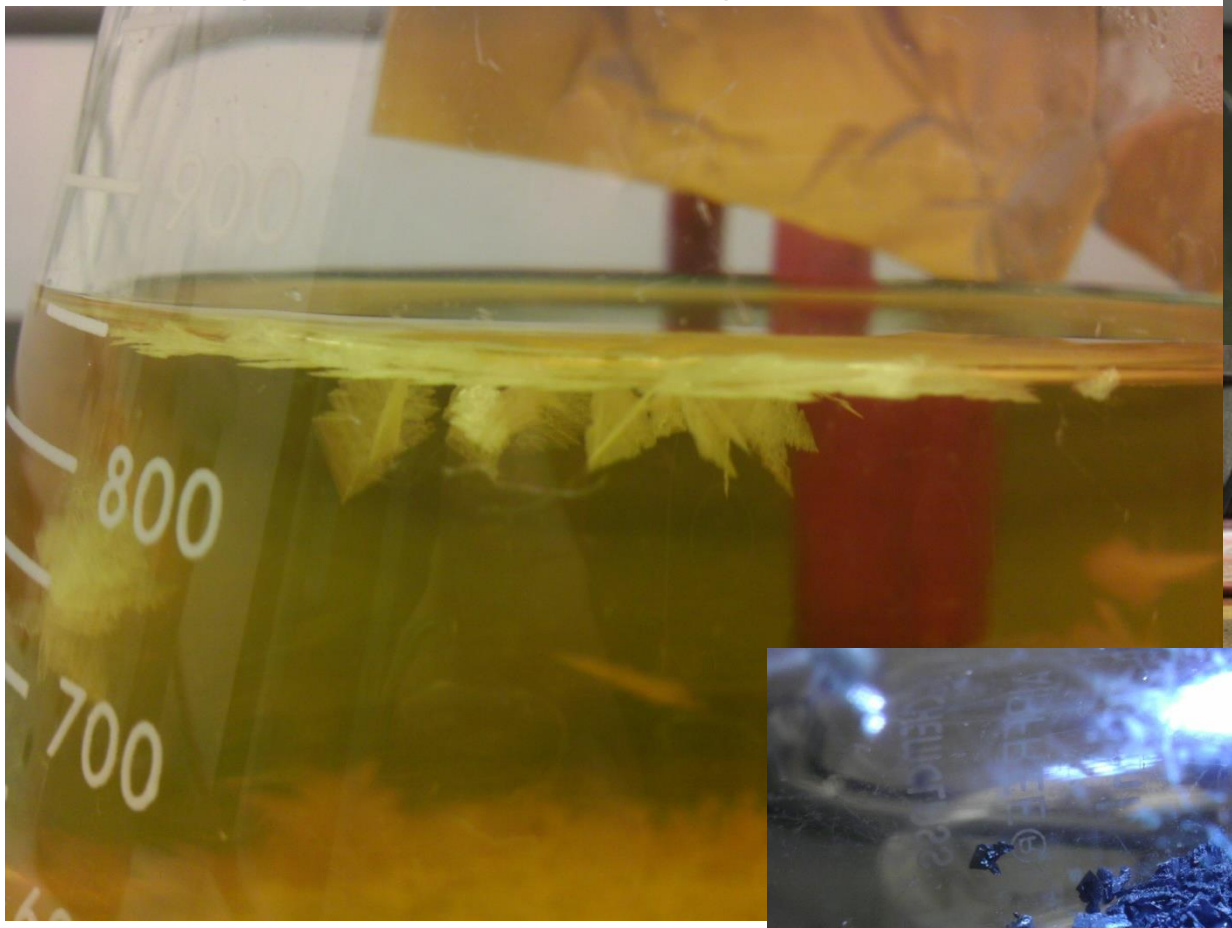


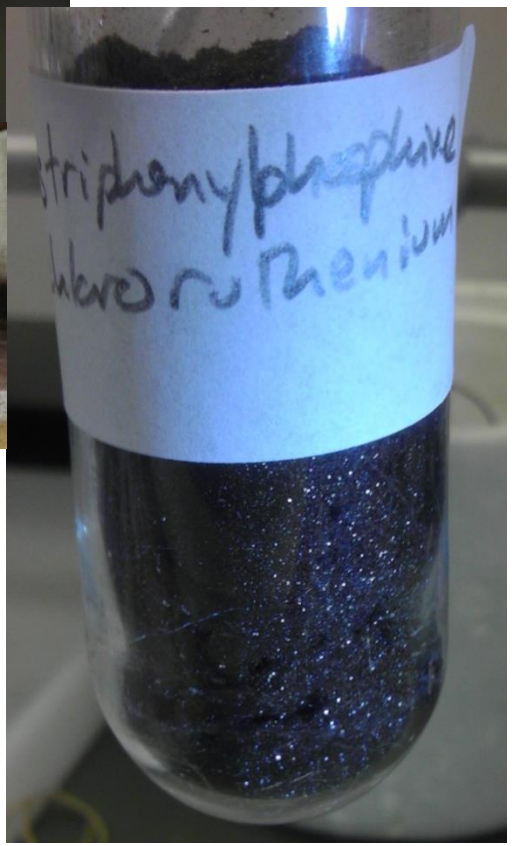
By original version: Haade;vectorization: Wjh31, Quibik - Vectorized from File:Interference of two waves.png, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=10073387

Interference and Nanostructures

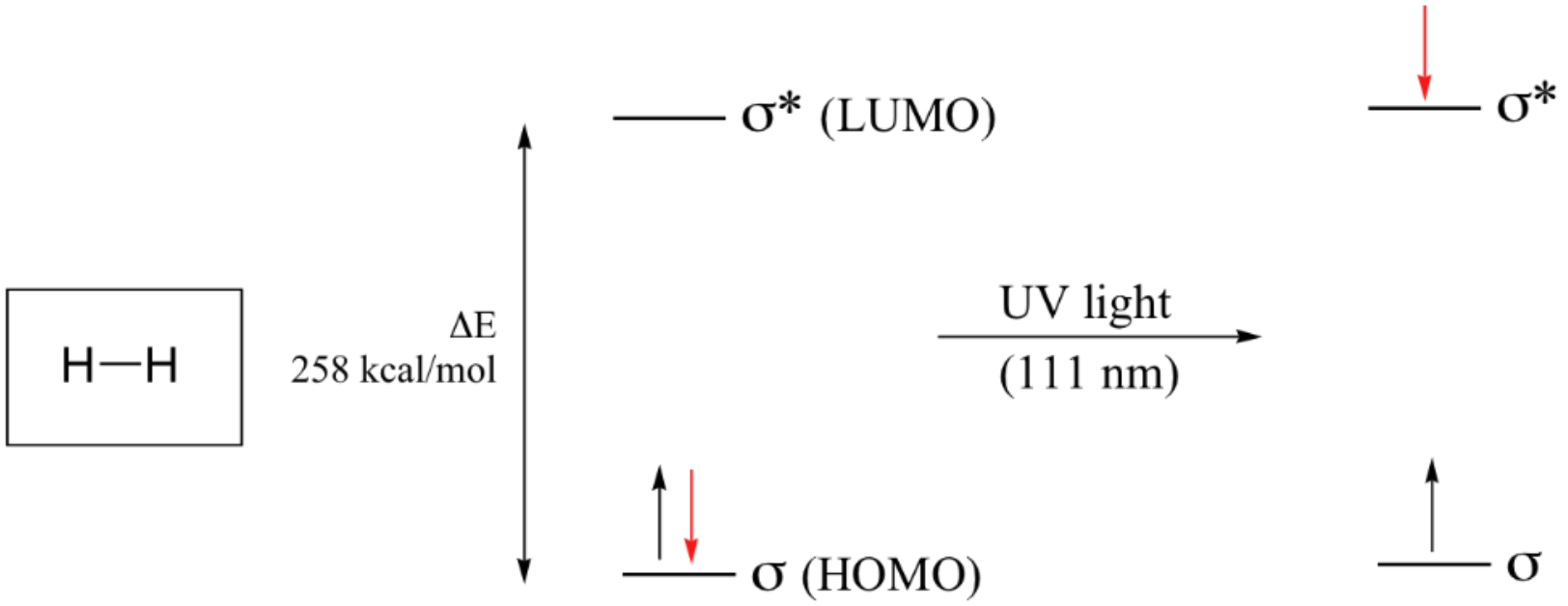
- Series of photographs in increasing magnification showing a butterfly and scale structure of butterfly wings
- https://en.wikipedia.org/wiki/File:Butterfly_magnification_series_collage.jpg

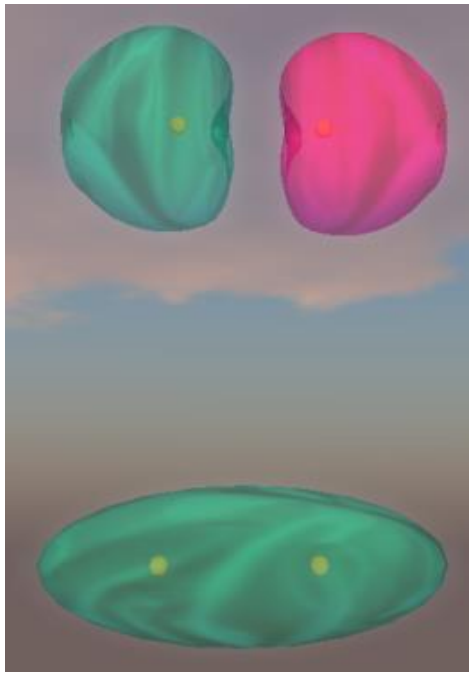
Speed Bump…





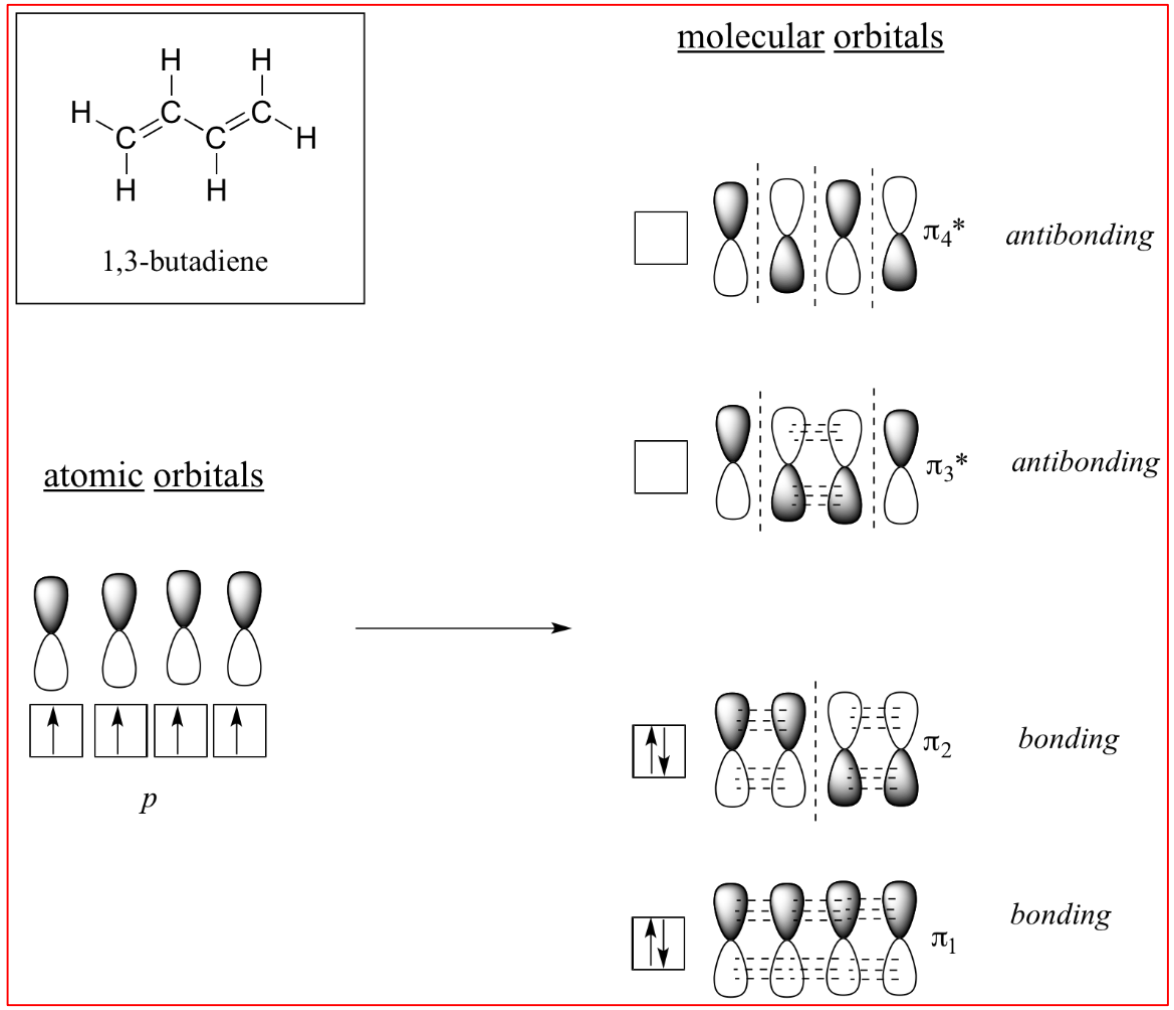
Electronic transitions in molecules

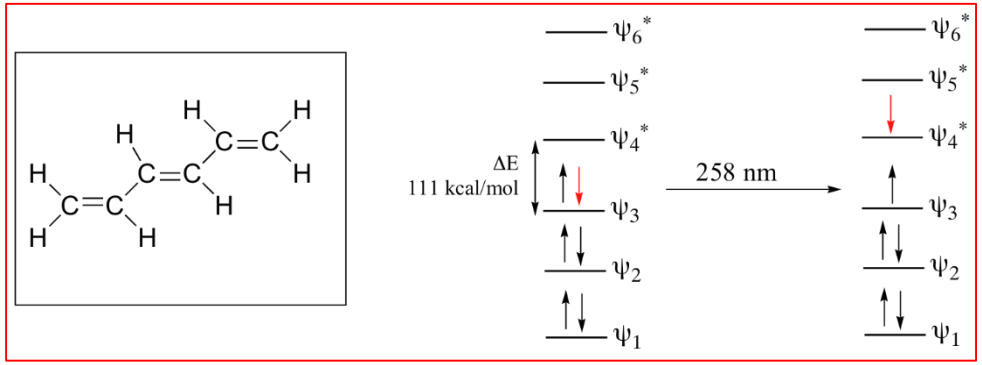


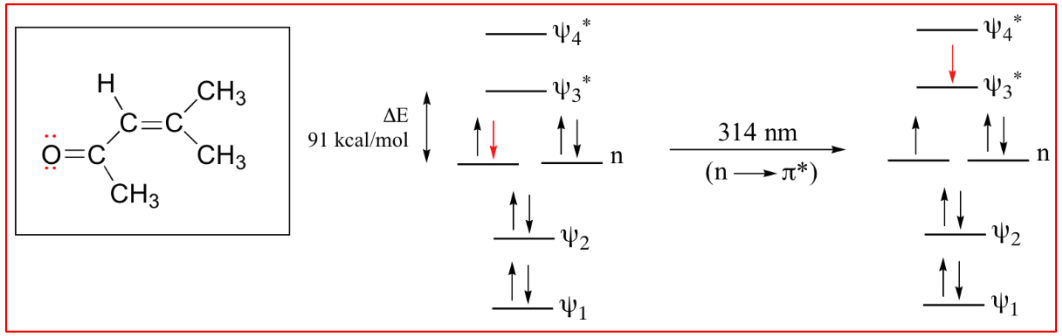


From
https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map%3A_Organic_Chemistry_(Vollhardt_and_Schore)/14%3A_Delocalized_Pi_Systems%3A_Investigation_by_Ultraviolet_and_Visible_Spectroscopy/14.11%3A_%09Electronic_Spectra%3A__Ultraviolet_and__Visible__Spectroscopy
Full attribution on "Electronic Spectra: Organic transitions LibreTexts license and attribution" slide

Transitions







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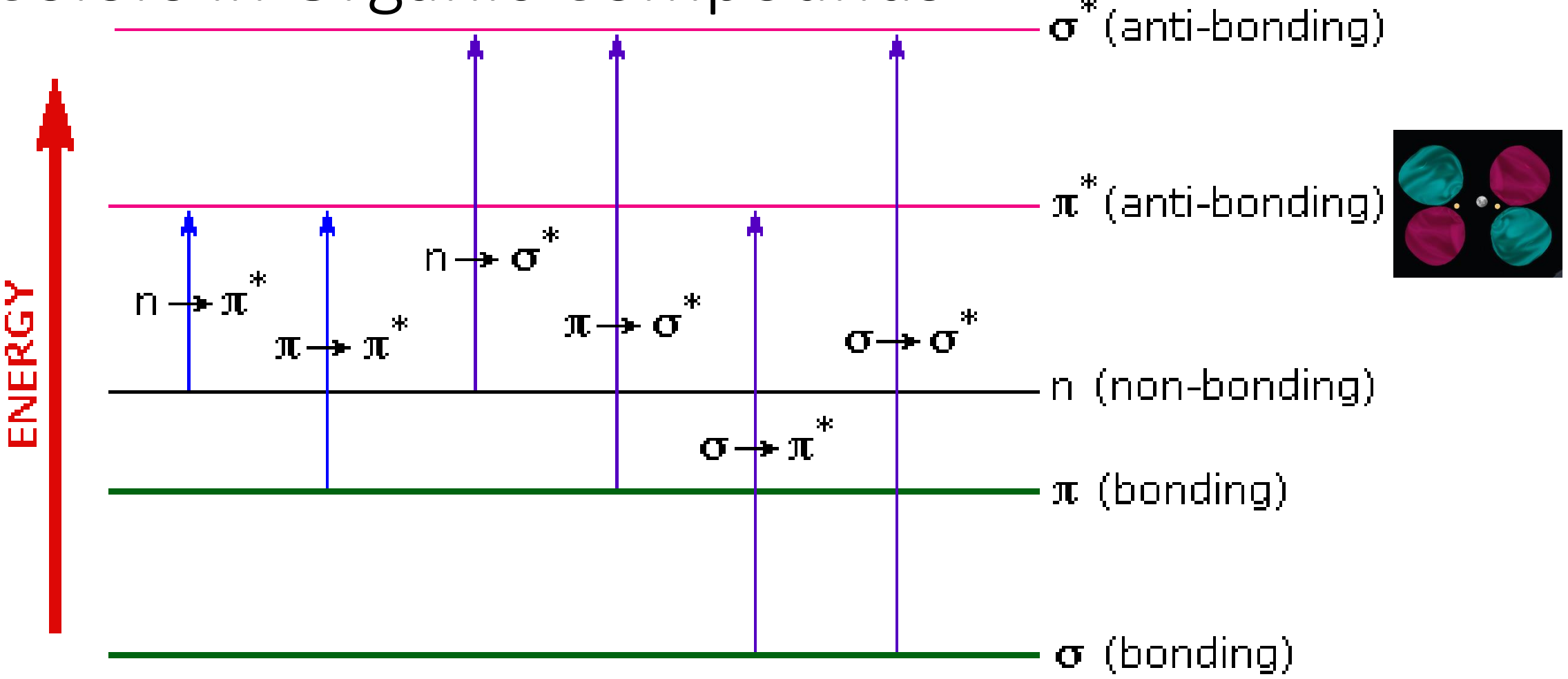
Colors in Organic Compounds



From
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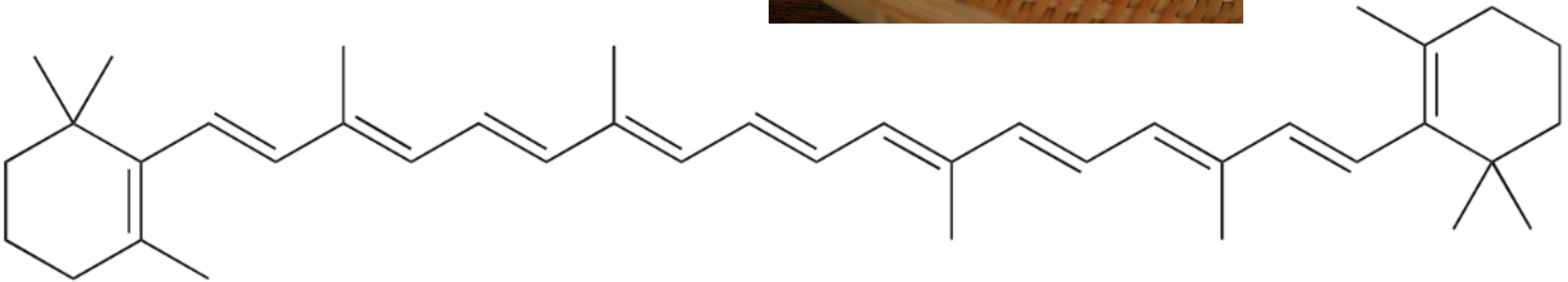
Lotsa bonds…



β-carotene

From
https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map%3A_Organic_Chemistry_(Vollhardt_and_Schore)/14%3A_Delocalized_Pi_Systems%3A_Investigation_by_Ultraviolet_and_Visible_Spectroscopy/14.11%3A_%09Electronic_Spectra%3A__Ultraviolet_and__Visible__Spectroscopy
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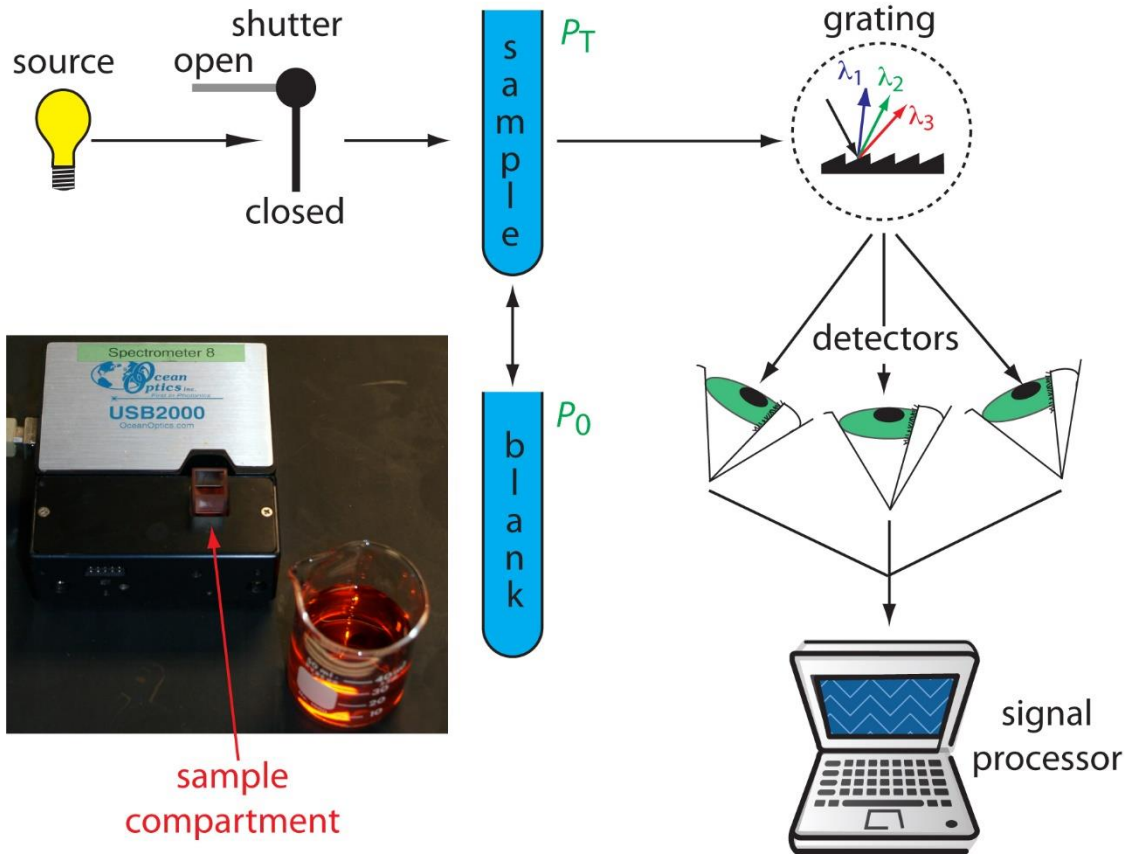
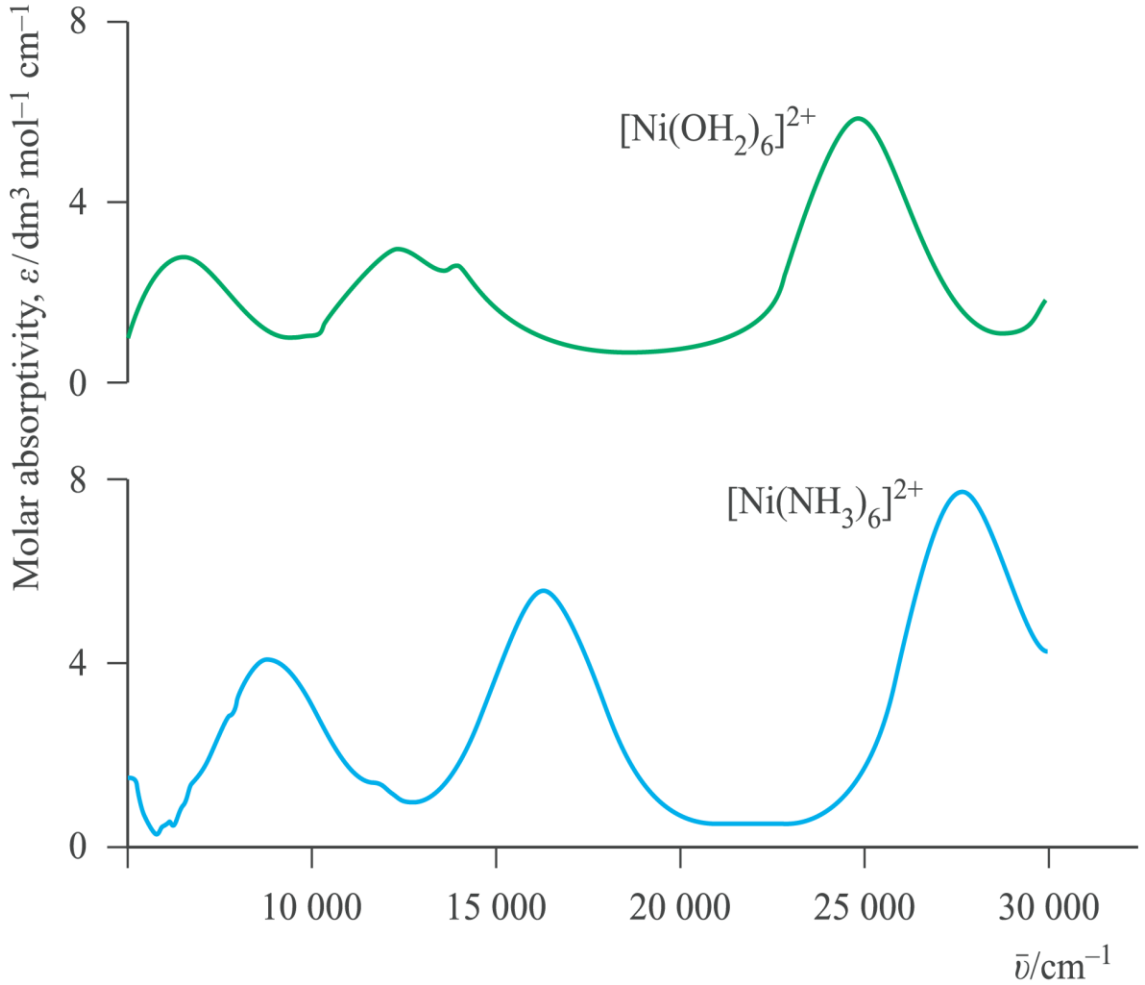
How do we study color?

- UV-VIS spectrometry
- Cartoon shows diode array spectrometer



21.23



E= hc/λ

Fig. 21.21 Electronic spectra of $[Ni(OH_2)_6]^{2+}$ (0.101 mol dm^{-3}) and $[Ni(OH_2)_6]^{2+}$ (0.315 mol dm^{-3} in aqueous NH_3 solution) showing three absorption bands. Values of the molar absorptivity, ε, are related to absorbance by the Beer–Lambert law (equation 21.12). [This figure is based on data provided by Christian Reber; see: M. Triest, G. Bussière, H. Bélisle and C. Reber (2000) *J. Chem. Ed.*, vol. 77, p. 670]

Copper solutions… various copper cations

$[Cu(H_2O)_6]^{2+}$
(not shown)

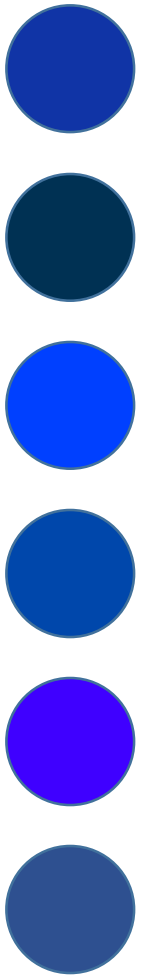
left
$[Cu(H_2O)_5(NH_3)]^{2+}$
$[Cu(H_2O)_4(NH_3)_2]^{2+}$
$[Cu(H_2O)_3(NH_3)_3]^{2+}$
$[Cu(H_2O)_2(NH_3)_4]^{2+}$
$[Cu(H_2O)(NH_3)_5]^{2+}$
right

I've had a variety of cat-ions….

Another bump

My Blue period…

- Egyptian Blue
- Prussian Blue
- Cerulean Blue
- Cobalt Blue
- Indigo
- YInMn Blue



Colours as assigned by Wikipedia's RGB values

I don't find them to be 100% representative… probably because monitors are limited in their ability to reproduce all the nuances of color

Shabti of Seti I , ca. 1294–1279 B.C.

- Faience
- “Egyptian Blue” first synthetic pigment
- $CaCuSi_4O_{10}$
- Source of copper in later times was bronze scraps, from traces of tin found in later examples.
- Recipe fell out of favour in Roman times, recently rediscovered.
- https://en.wikipedia.org/wiki/Egyptian_blue

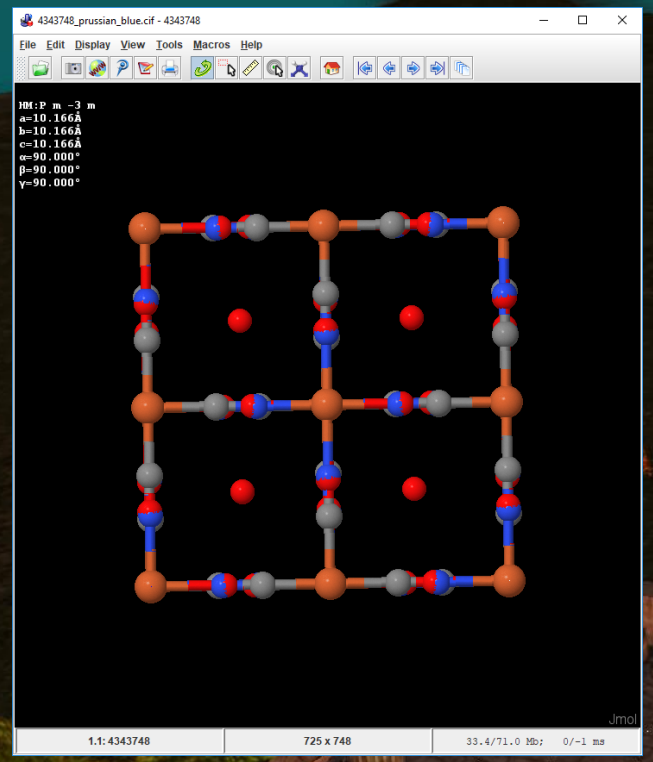
prize/trophy / Panathenaic amphora, , object 1856,1001.1, The Metropolitan Museum of Art
Image 1 of 7
https://www.metmuseum.org/art/collection/search/544763#

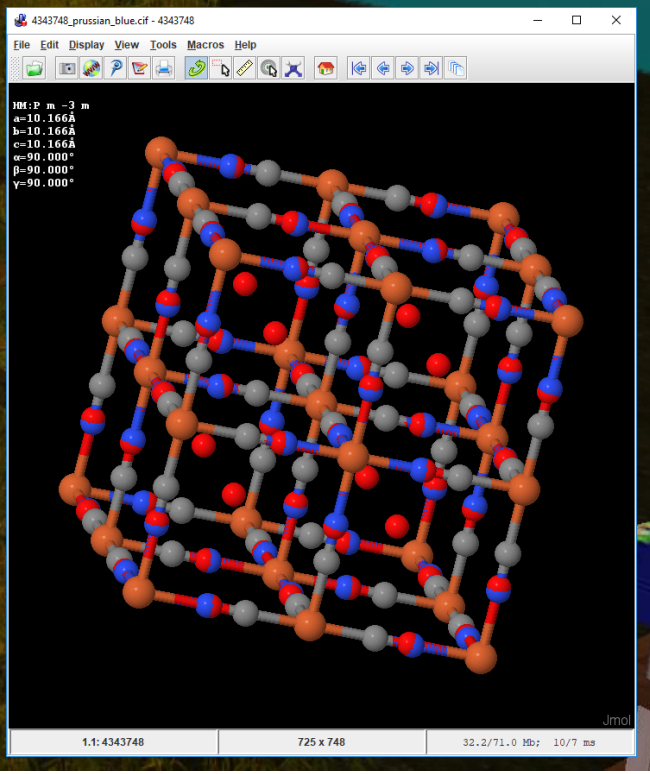
A Starry Night, Vincent Van Gogh, 1889

- Prussian Blue and Cerulean Blue
  - $Fe_4[Fe(CN)_6]_3$
- “Cerulean” is a cobalt (II) stannate
- Prussian Blue discovered 1708 or so… nontoxic, despite all the cyanide
- See structure model…

Museum of Modern Art, New York City
https://en.wikipedia.org/wiki/File:Vincent_van_Gogh_Starry_Night.jpg

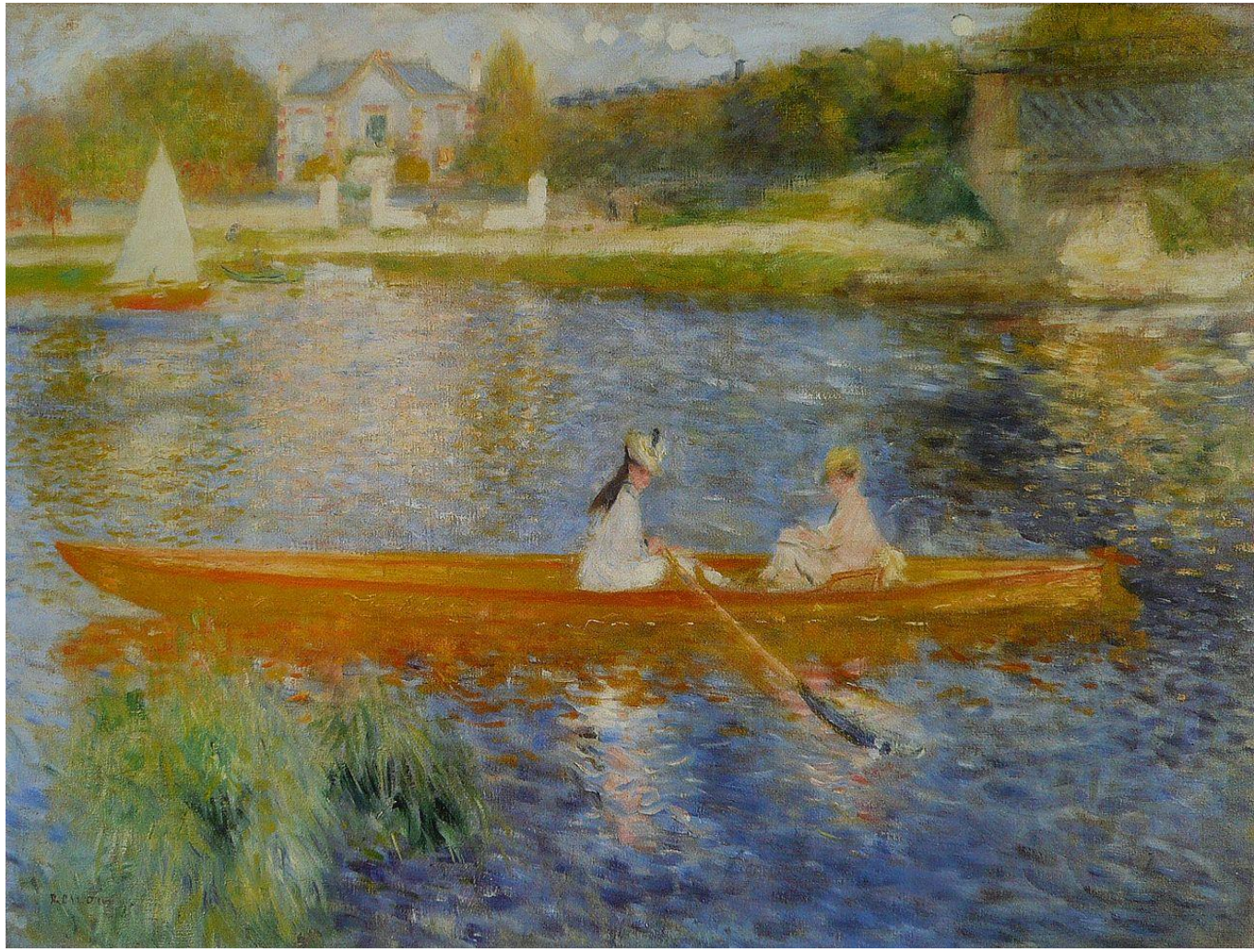
Prussian Blue skeleton….





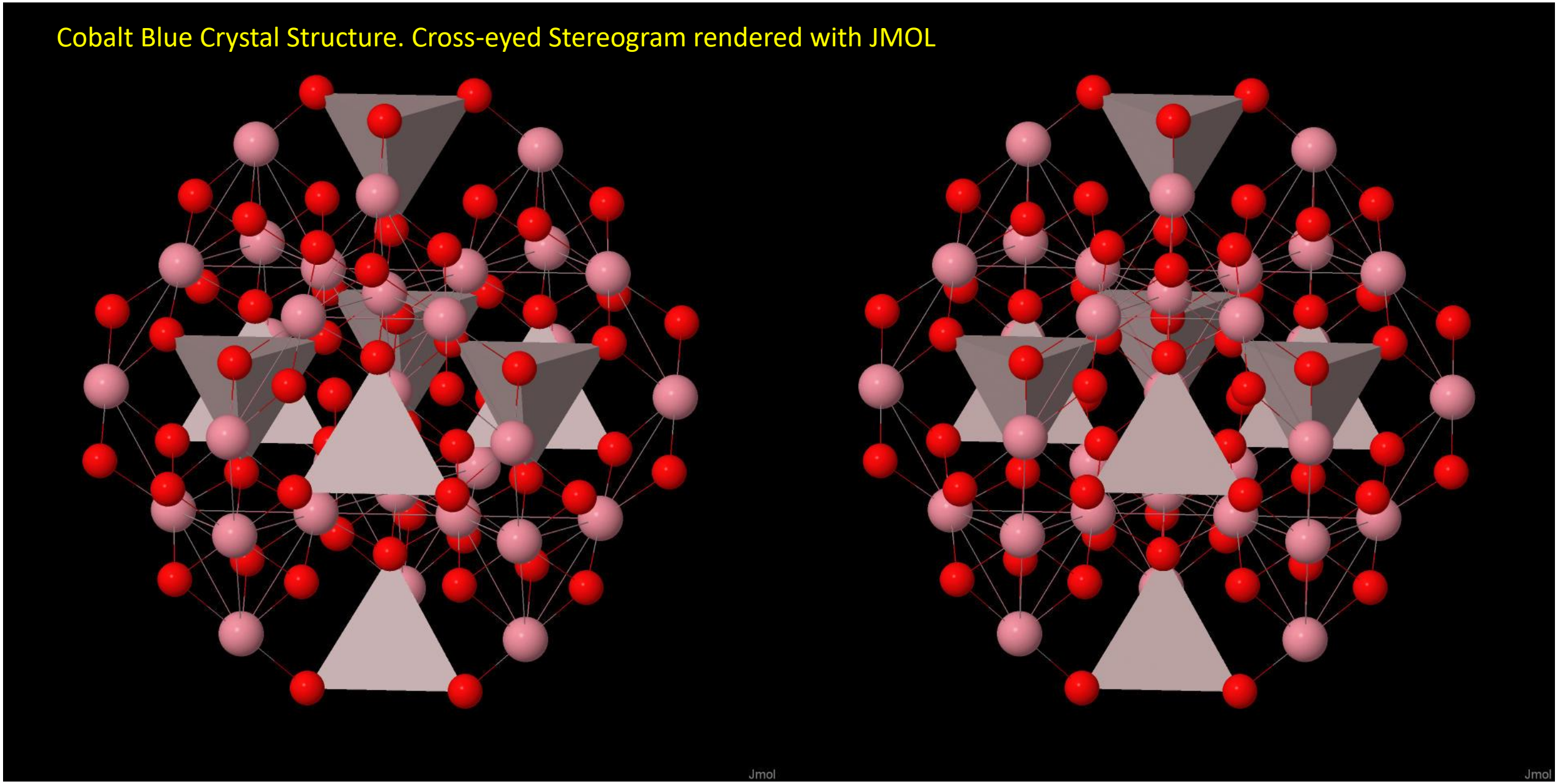
Boating on the Seine (La Yole), c. 1879
Pierre-Auguste Renoir

- Cobalt Blue
- Cobalt Aluminate $Co_2Al_2O_4$
- Co is kinda toxic…



The National Gallery, London, UK.
http://www.nationalgallery.org.uk/paintings/pierre-auguste-renoir-the-skiff-la-yole

Cobalt Blue Crystal Structure. Cross-eyed Stereogram rendered with JMOL



Bosi F, Halenius U, D'Ippolito V, Andreozzi G B, "Blue spinel crystals in the $MgAl_2O_4$-$CoAl_2O_4$ series: Part II. Cation ordering over short-range and long-range scales," *American Mineralogist* 97 (2012) 1834-1840.

Kimono

- Summer kimono, resist-dyed in **indigo** with a pattern of birds, bamboo and flowers. Made of dyed, painted and embroidered silk.
- Made in Japan, ca 1820

The British Museum, Museum number 1979,0411.2
https://www.britishmuseum.org/research/collection_online/collection_object_details/collection_image_gallery.aspx?assetId=820898001&objectId=766988&partId=1

Indigo

- Indigo is a naturally-occurring organic dye
  - The other blues presented today are pigments

https://artsandculture.google.com/asset/indigofera-tinctoria-cultivation-in-uttarakhand/VwHP5FK7XVElSw

https://artsandculture.google.com/asset/freshly-cut-indigofera-leaves-are-soaked-in-water/WgGCAJtXOqR-ig?childAssetId=-QGWRex58A1dYg

https://artsandculture.google.com/asset/indigofera-soaking-in-the-water/WgGCAJtXOqR-ig?childAssetId=HwFzTF2blwiRWg

https://artsandculture.google.com/asset/indigofera-soaking-in-the-water/WgGCAJtXOqR-ig?childAssetId=BQHAu2ykpfAODA

Google Arts and Culture series of photos on Indigofera Tinctoria Cultivation in Uttarakhand, India

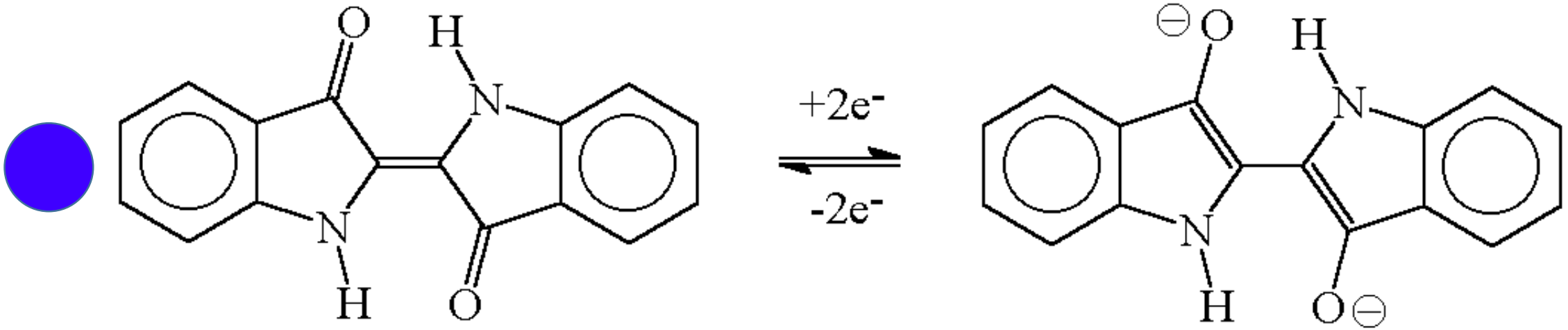
Indigo has 2 forms… can make the soluble “leuko” form by reduction, including by fermentation.

Allowing cloth soaked with the soluble, colorless form to dry in air re-oxidizes the dye to the insoluble, colorfast blue form….

Indigo

Need high pH to keep dianion from getting protonated… not soluble and not colored.

- Indigo is a naturally-occurring organic dye
  - Most indigo is produced artificially today
  - Synthesis from coal tar discovered in late 1800's by Scheele



$$2\ C_{16}H_{10}N_2O_2^{2-} + O_2 + 2H_2O \rightarrow 2\ C_{16}H_{10}N_2O_2 + 4\ OH^- \qquad \Delta E° = 0.14V$$

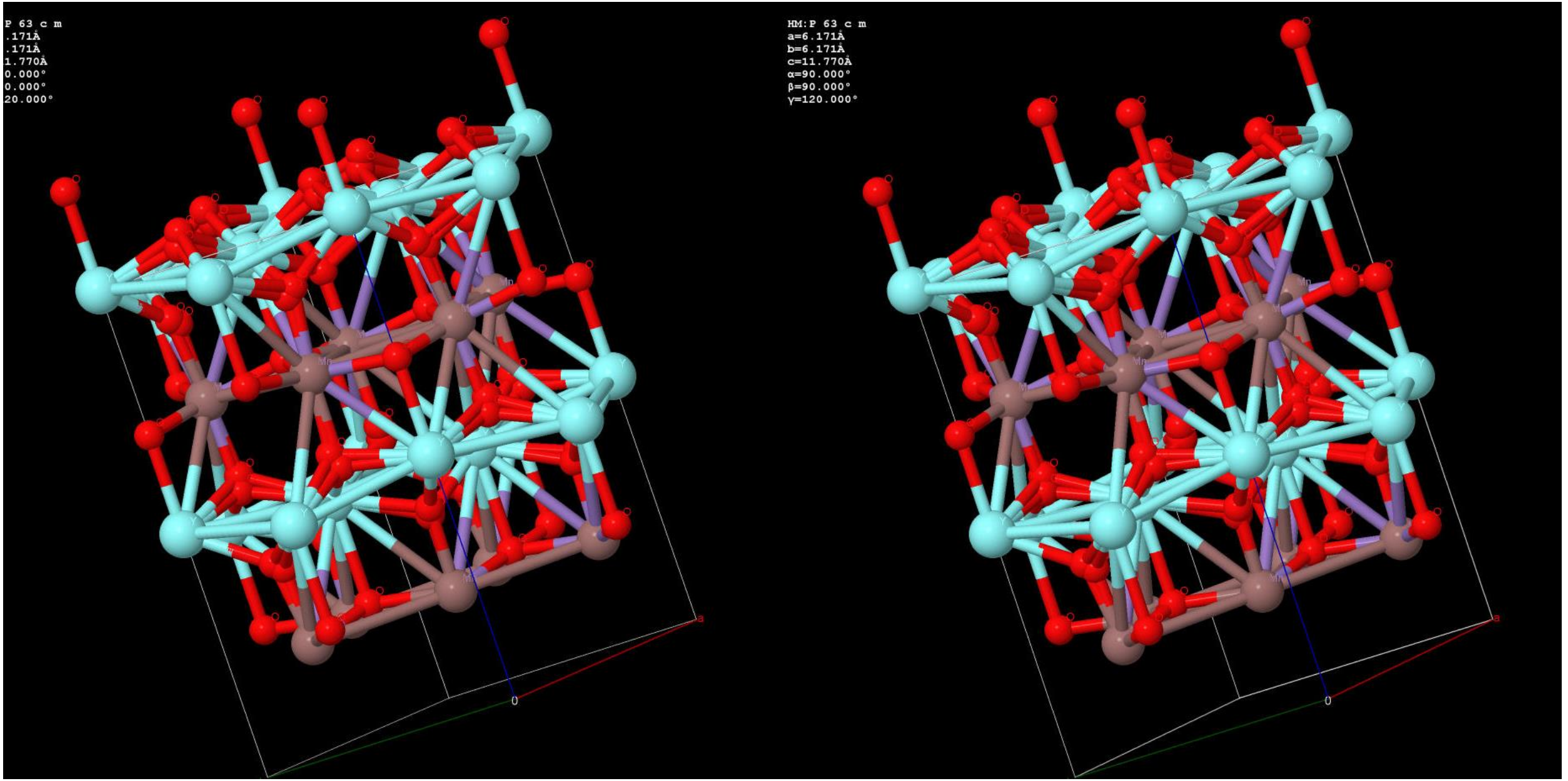
YInMn Blue discovered 2009

- $YIn_{1-x}Mn_xO_3$
- First new blue in 200 years
- Apparently nontoxic
- Also has high reflectance in near-IR (900-2000 nm) region
- Discovered by Mas Subramanian at Oregon State U. as part of his NSF-sponsored research
- Color has been commercialized, close to cobalt blue

Photograph of YInMn Blue as synthesized in the laboratory, photo by Mas Subramanian
https://en.wikipedia.org/wiki/YInMn_Blue#/media/File:YInMn_Blue_-_cropped.jpg

$In_{0.37}Mn_{0.63}O_3Y$

http://www.crystallography.net/cod/4105420.html



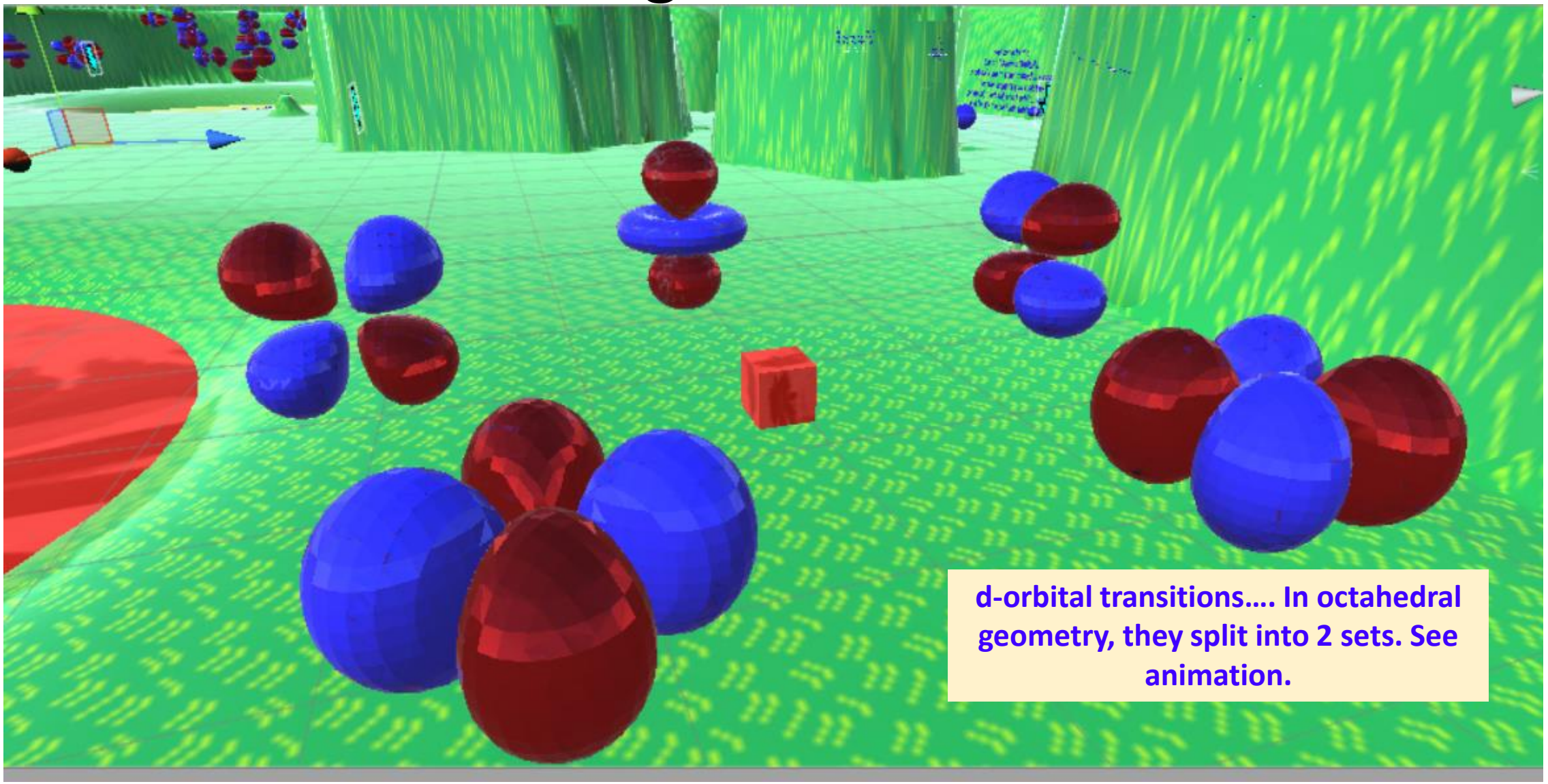
Andrew E. Smith; Hiroshi Mizoguchi; Kris Delaney; Nicola A. Spaldin; Arthur W. Sleight; M. A. Subramanian," Mn^{3+} in Trigonal Bipyramidal Coordination: A New Blue Chromophore," *Journal of the American Chemical Society* **2009**, *131*, 17084 - 17086

Inorganic pigments for stained glass…

- Silver ions for yellow and shades of grey
- A topic for the future….

World War I Memorial stained glass window, Trinity Church, Cowansville, Quebec Canada. Photo credit: me!

Where do the inorganic colors come from?



Symbols

H L=5
G L=4
F L=3
D L=2
P L=1
S L=0

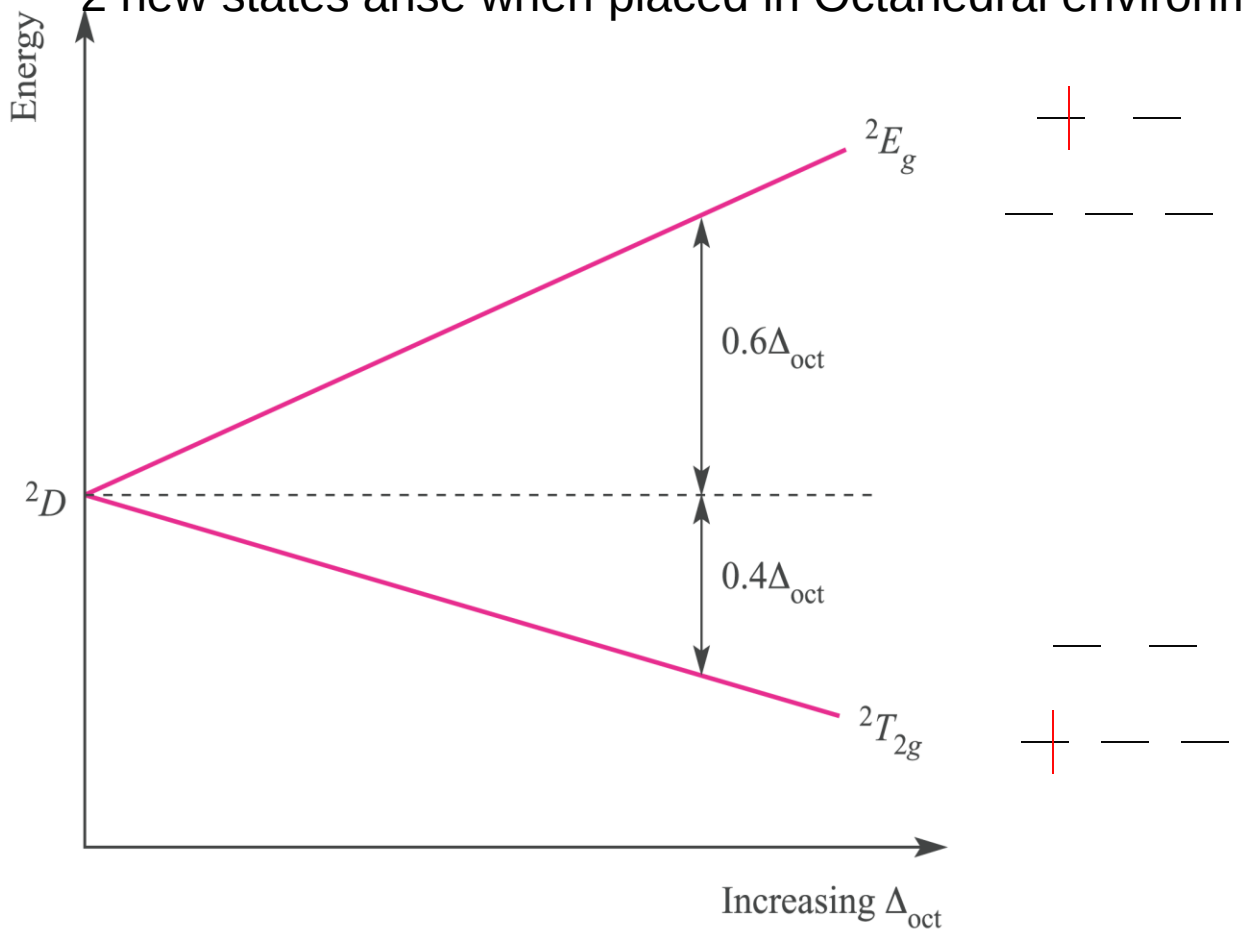
Superscript

unpaired +1

^{2}D: 1 e$^-$ in 5 d-orbitals: highest M_L =2

Doublet spin state

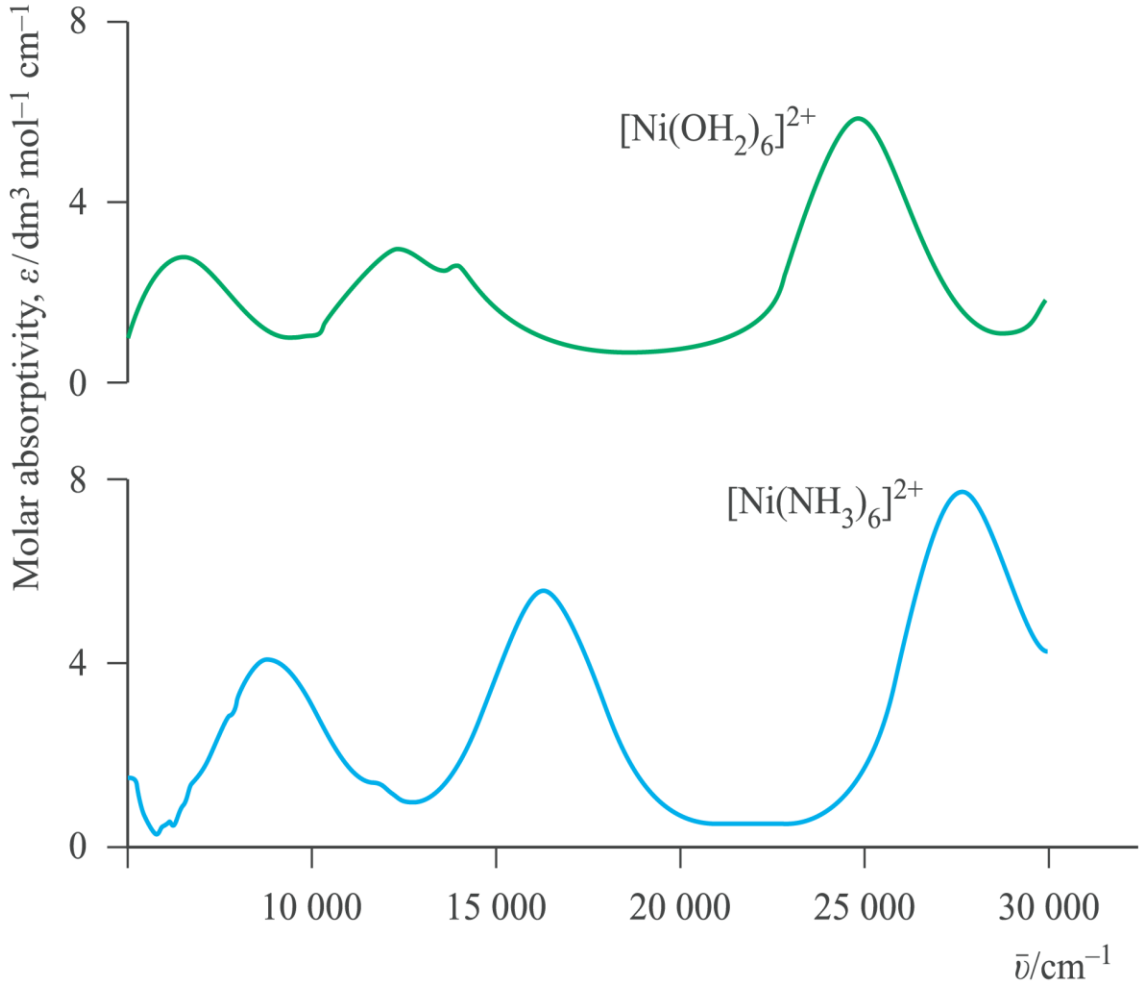
2 new states arise when placed in Octahedral environment



E= hc/λ

Fig. 21.18 Energy level diagram for a d^1 ion in an octahedral field.

21.23



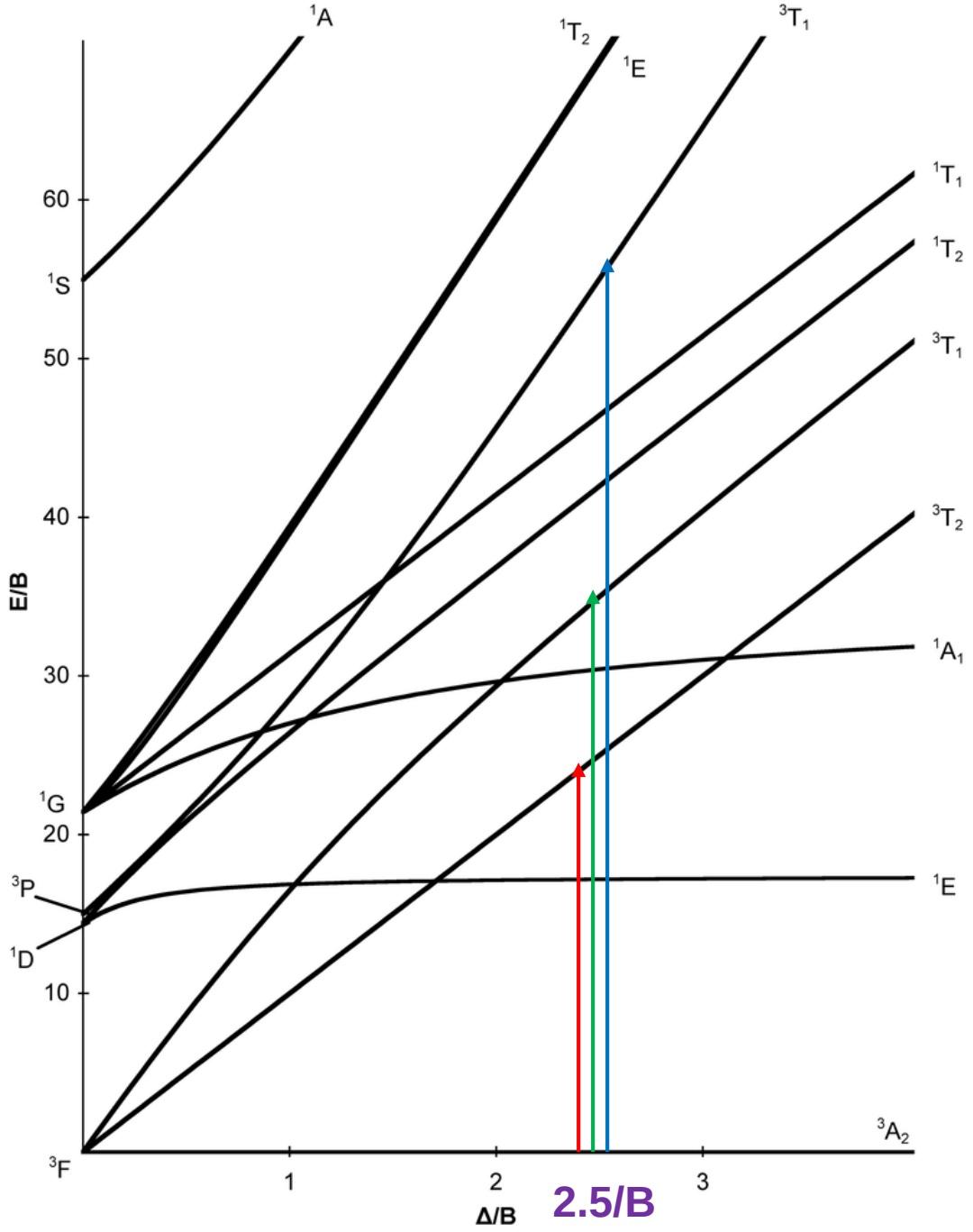
E= hc/λ

Fig. 21.21 Electronic spectra of $[Ni(OH_2)_6]^{2+}$ (0.101 mol dm^{-3}) and $[Ni(OH_2)_6]^{2+}$ (0.315 mol dm^{-3} in aqueous NH_3 solution) showing three absorption bands. Values of the molar absorptivity, ε, are related to absorbance by the Beer–Lambert law (equation 21.12). [This figure is based on data provided by Christian Reber; see: M. Triest, G. Bussière, H. Bélisle and C. Reber (2000) *J. Chem. Ed.*, vol. 77, p. 670]

d^8

Ni(II) is d^8. Use the diagram at right.

- $^3A_2$ is ground state… only allowed transitions are to where there is a superscript 3 to left of term symbol.
- $^3A_2 \rightarrow {}^3T_2$
  $^3A_2 \rightarrow {}^3T_1$
  $^3A_2 \rightarrow {}^3T_1$ (up high)



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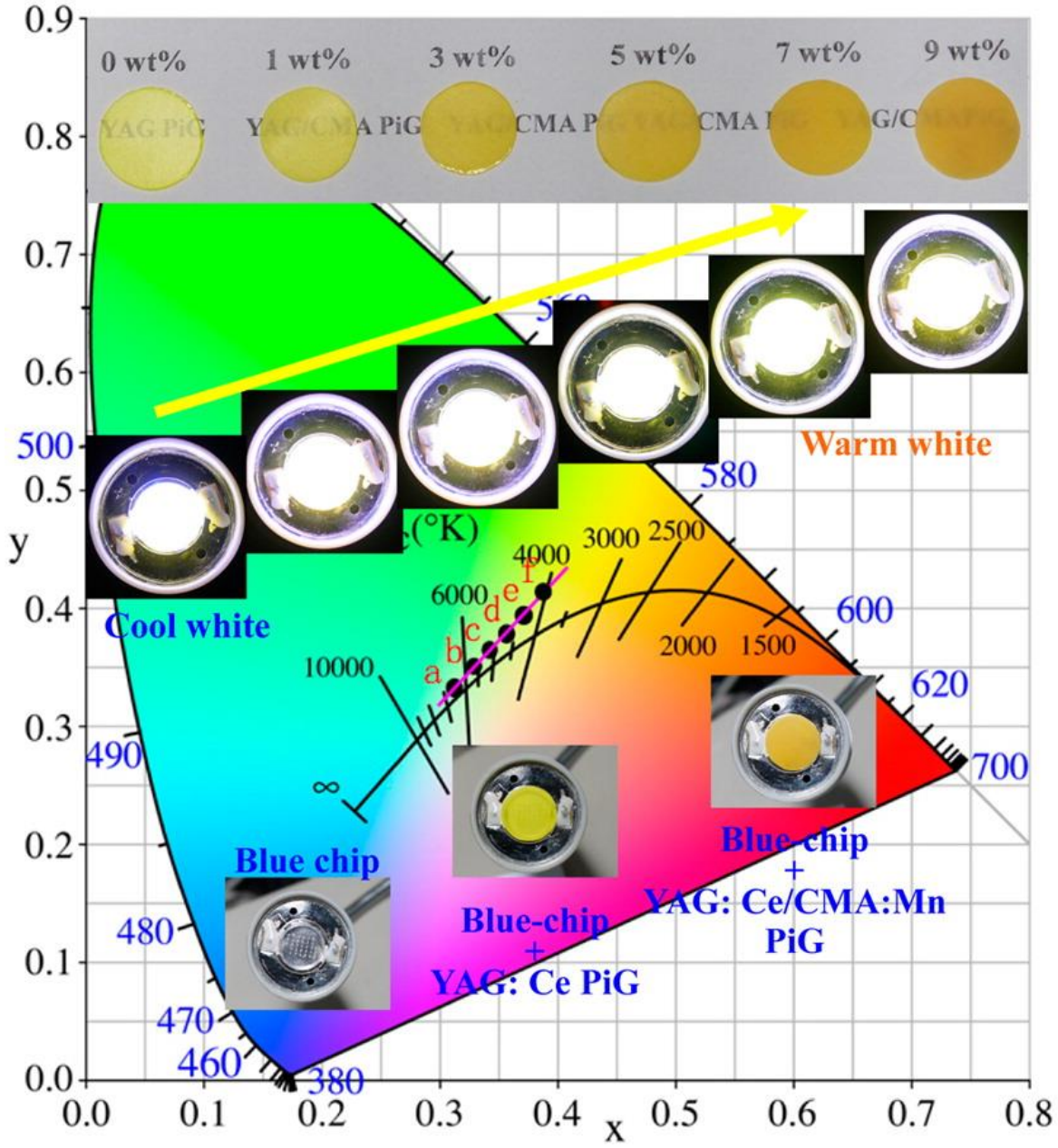
A topic for the future…

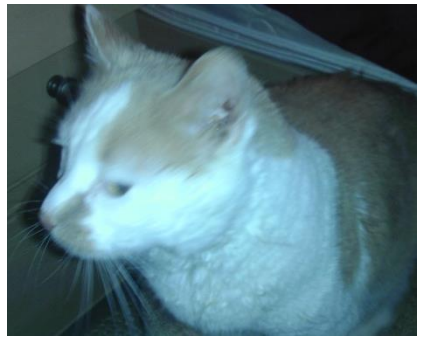
Light emitting diode research is often summarized with color vs. composition diagrams… especially when the goal is to create a white-light LED



CIE chromaticity diagram of w-LEDs fabricated by coupling 5 wt % YAG:Ce3+ and *y* (*y* = 0, 1, 3, 5, 7, 9) wt % CMA:Mn4+ embedded PiG with blue chips; insets show photographs of the PiG samples with varied CMA:Mn4+ weighted contents, the corresponding LED packages and their electroluminescence driven by a 350 mA current.

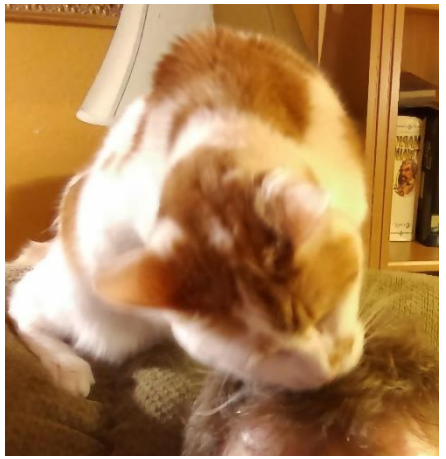
Published in: Bo Wang; Hang Lin; Ju Xu; Hui Chen; Yuansheng Wang; *ACS Appl. Mater. Interfaces* **2014,** 6, 22905-22913.
DOI: 10.1021/am507316b

Thanks!



- Members and Students of the Science Circle!
- Students and Faculty of Dept. of Chem., SIUE.
- Generous support of National Science Foundation for our work on heme-nitrosyl complexes, NSF-CHE 1566509
- DPA-LLC for hosting animated gifs and other files on their website

- My cats for their patience…



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Organic Chromophores

- See Woodward Rules (https://en.wikipedia.org/wiki/Woodward%27s_rules)
- Good description of delocalized organic pi-systems at: https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map%3A_Organic_Chemistry_(Vollhardt_and_Schore)/14%3A_Delocalized_Pi_Systems%3A_Investigation_by_Ultraviolet_and_Visible_Spectroscopy
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Single Crystal X-Ray Diffraction

- Gives a “snapshot” of molecular structure
- Very useful when “sporting” methods like IR and NMR aren’t enough.
- Can now use for largish bio-molecules to study drug-receptor interactions

- Open source access via:
- http://www.crystallography.net/cod/index.php
- http://rruff.geo.arizona.edu/AMS/amcsd.php
- http://www.rcsb.org/pdb/home/home.do

Small molecule
American Minerologist site
Protein Crystallography site

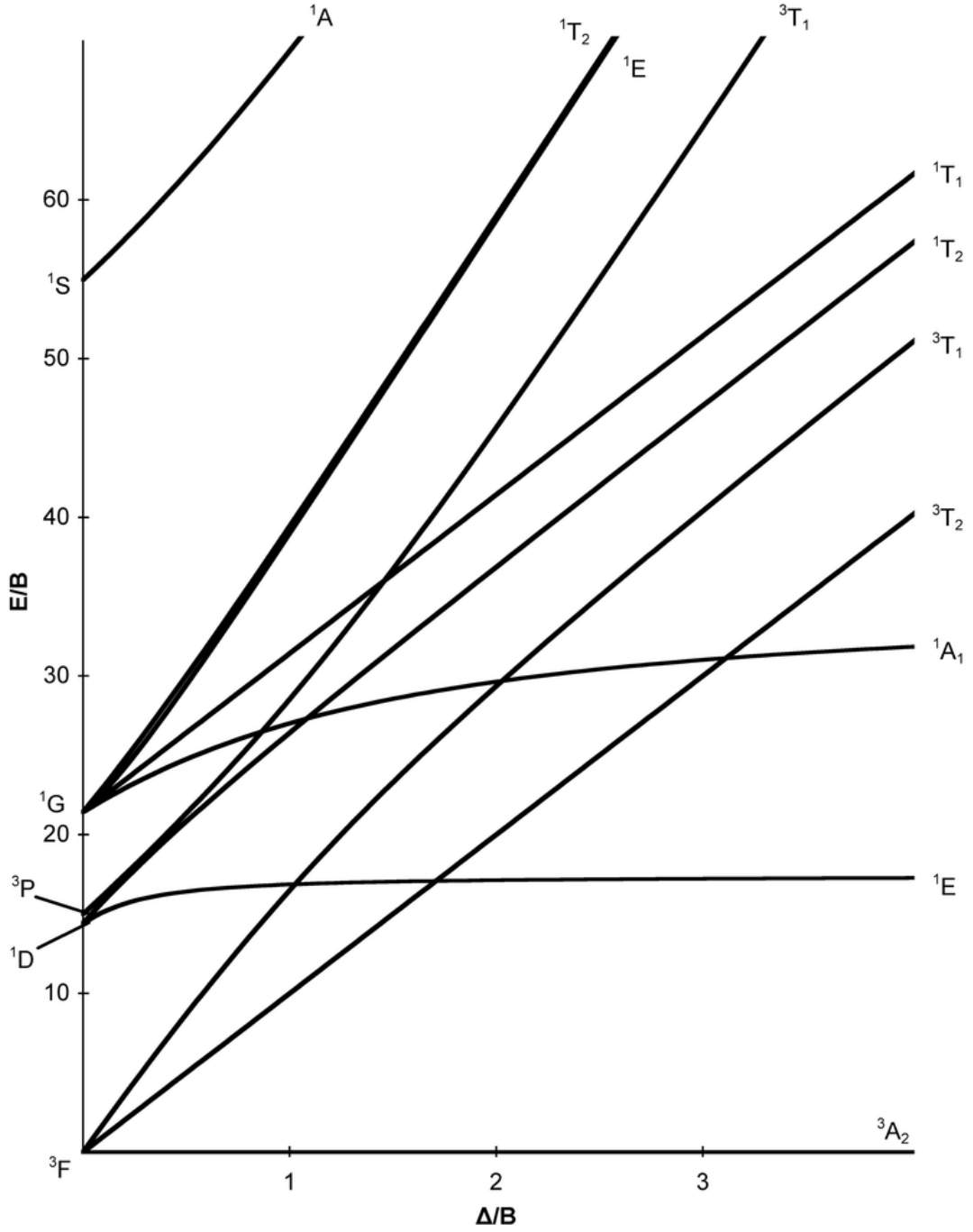
Convenient

- Can use JMOL (http://jmol.sourceforge.net/) to view “cif” files, eport as X3D files
- Can use Blender to edit (remove atoms inside of other atoms) and then export as DAE files
- Can import DAE files into Second Life.

d^8... Like Ni^{2+} (green)

Good diagrams on Wikipedia…

https://en.wikipedia.org/wiki/Tanabe%E2%80%93Sugano_diagram



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