Inorganic

Orbitals interactions in metals: Pigmentation and Absorption Spectra

Last Time

- Crystal field splitting for other geometries

- Tetrahedral crystal field stabilization energies

- Periodic trends in the stabilities of transition metal compounds

- The Irving Williams Series

Lecture Topics

- Pigments and the chemistry of color

- Electronic transitions in chemistry

- UV-vis absorption spectroscopy

- Molar Absorptivity

- Types of electronic transitions in metal complexes

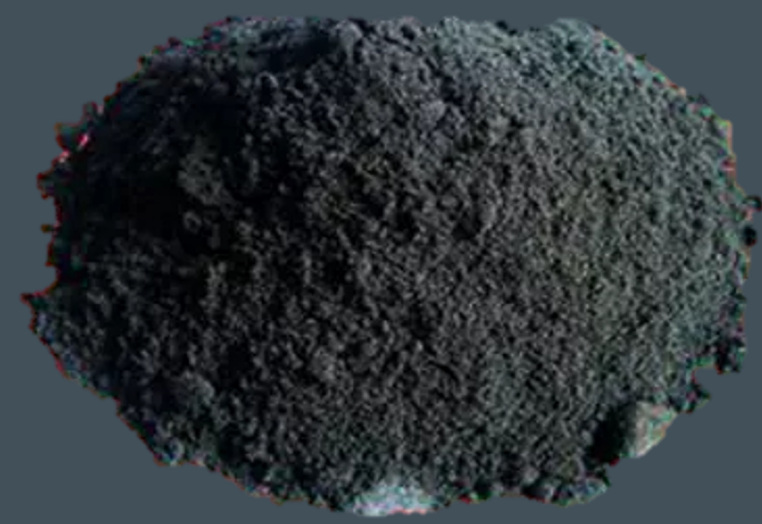- Selection Rules and Molar Absorptivity

Spectral Features

A characteristic feature of many *d*-block metal complexes is their colors, which arise because they absorb light in the visible region.
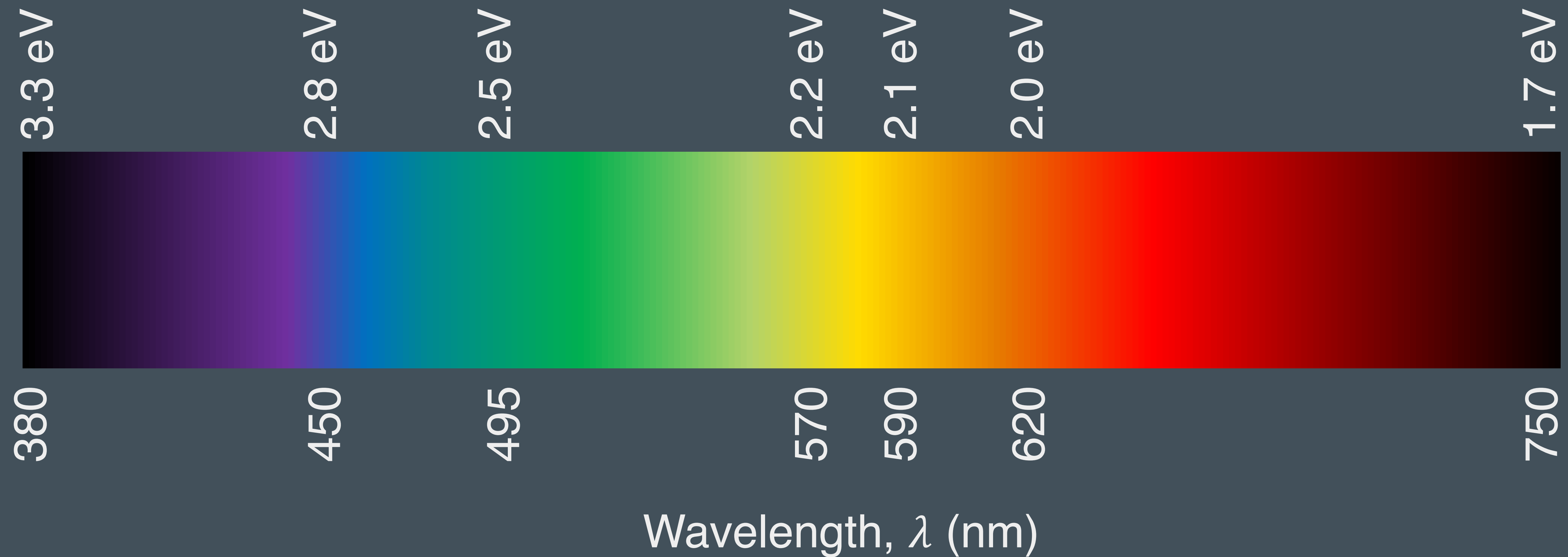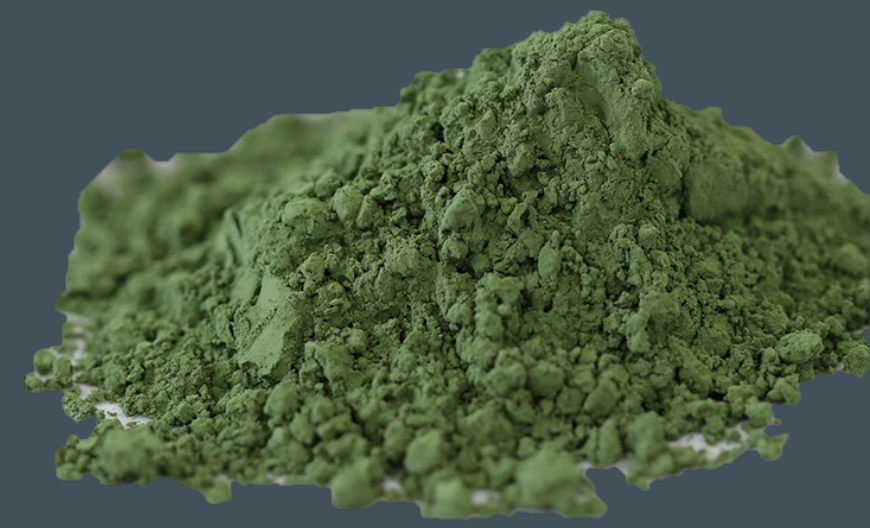

Wavelength, λ (nm)
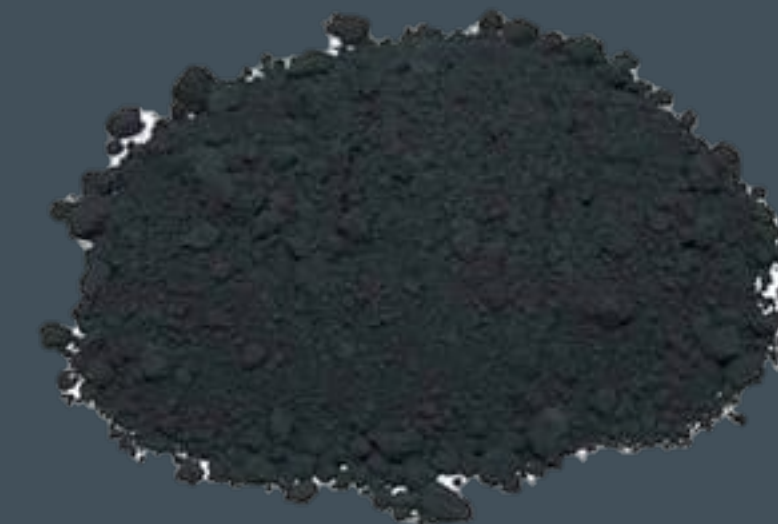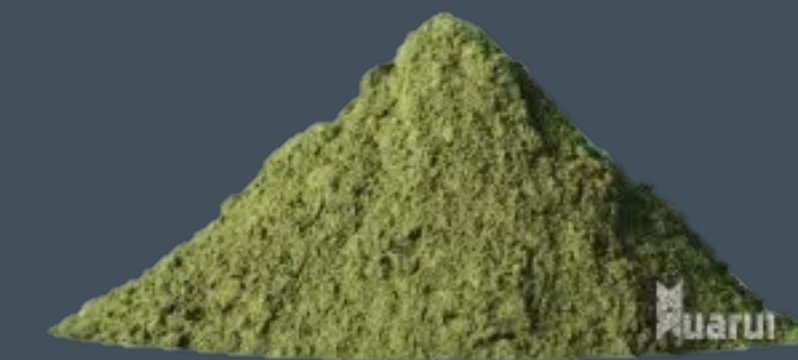
Pigments

TiO_2

VO_2

Cr_2O_3

MnO

Fe_2O_3

CoO

NiO
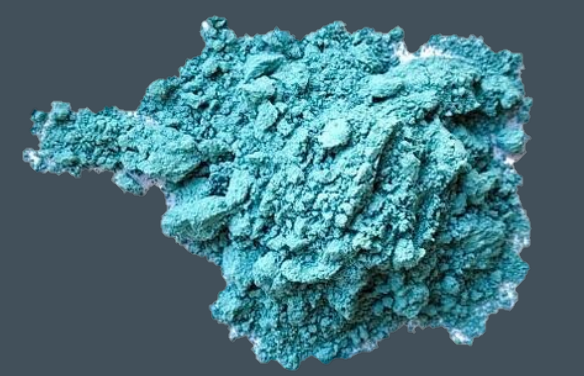
$Cu(OH)_2$

Ti_2O_3

V_2O_5

$K_2Cr_2O_7$
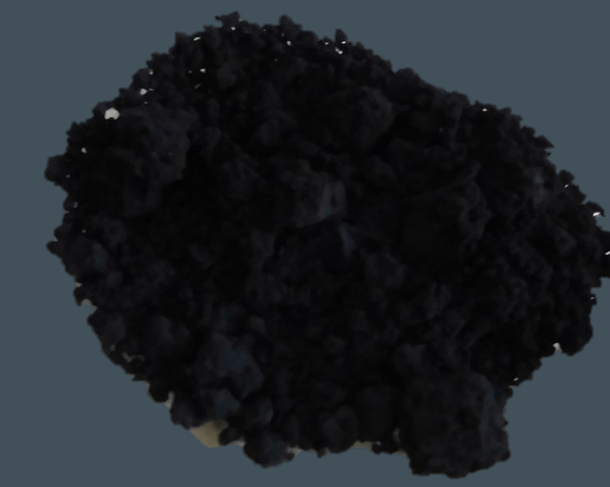
Fe_3O_4
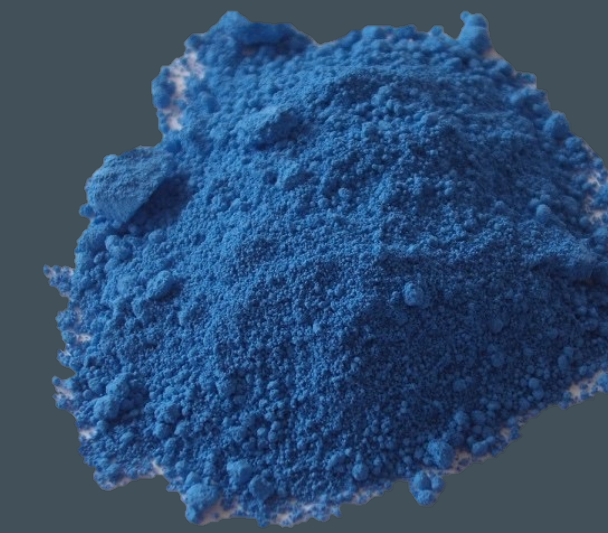
$CoAl_2O_4$

Ni_2O_3
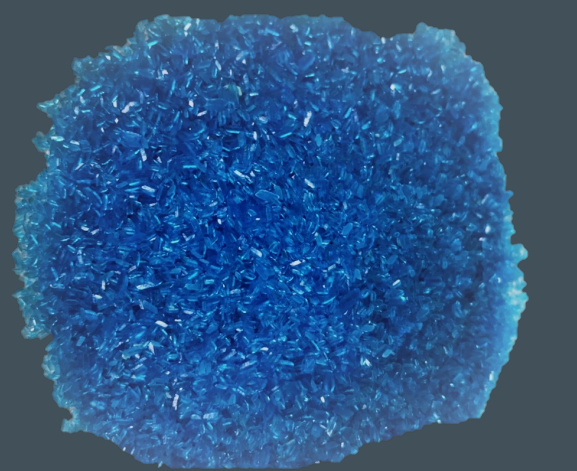
$CuSO_4$

$Co_3(PO_4)_2$

How pigments work

Incident white light

Absorb all wavelengths

Appears white

TiO_2 does not absorb at any visible wavelength

TiO_2

How pigments work

Incident
white light

Absorb all wavelengths

Appears black

*Carbon absorbs all
wavelengths*

Carbon black

How pigments work

Incident
white light

Absorb nearly all but green
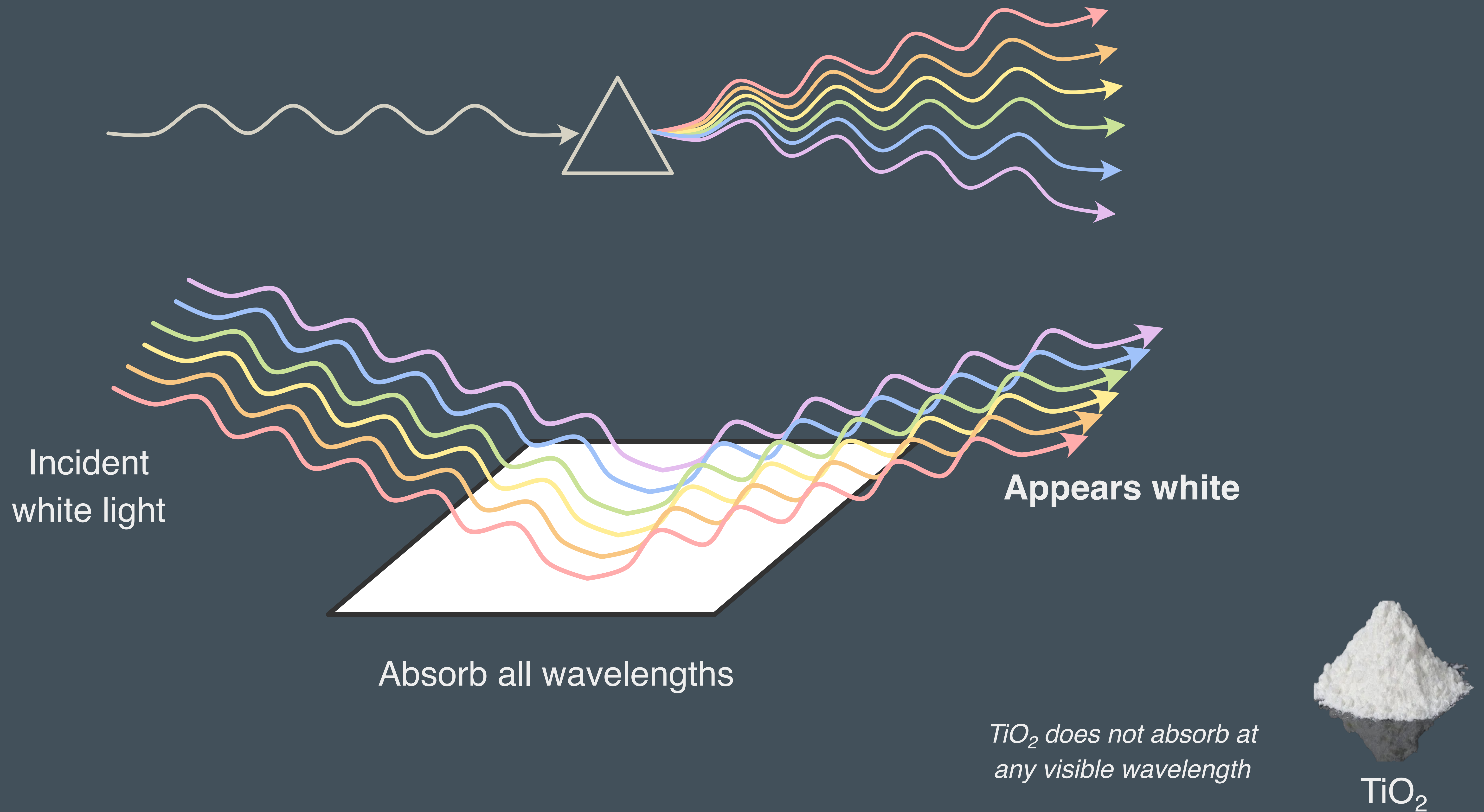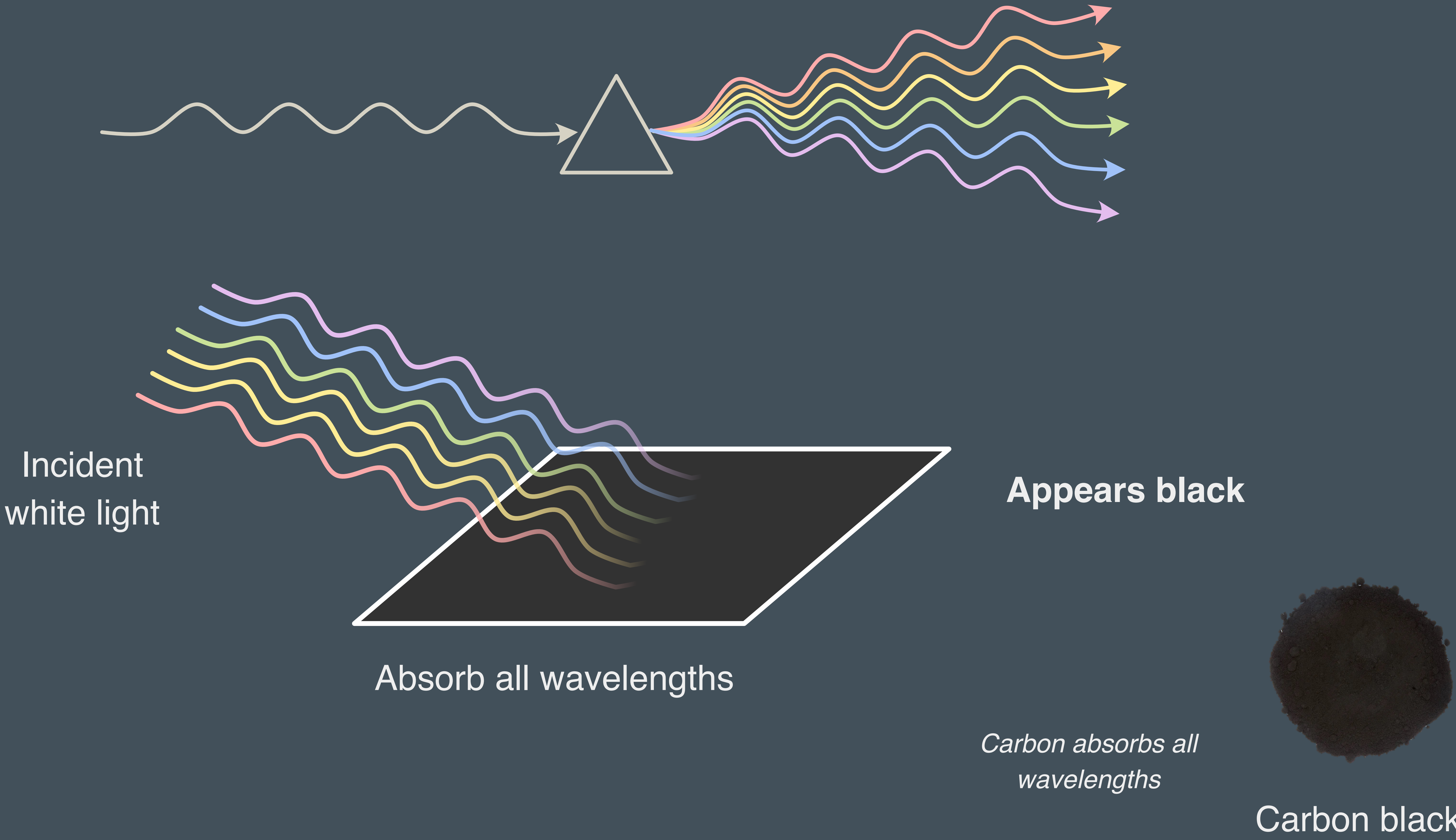
Appears black
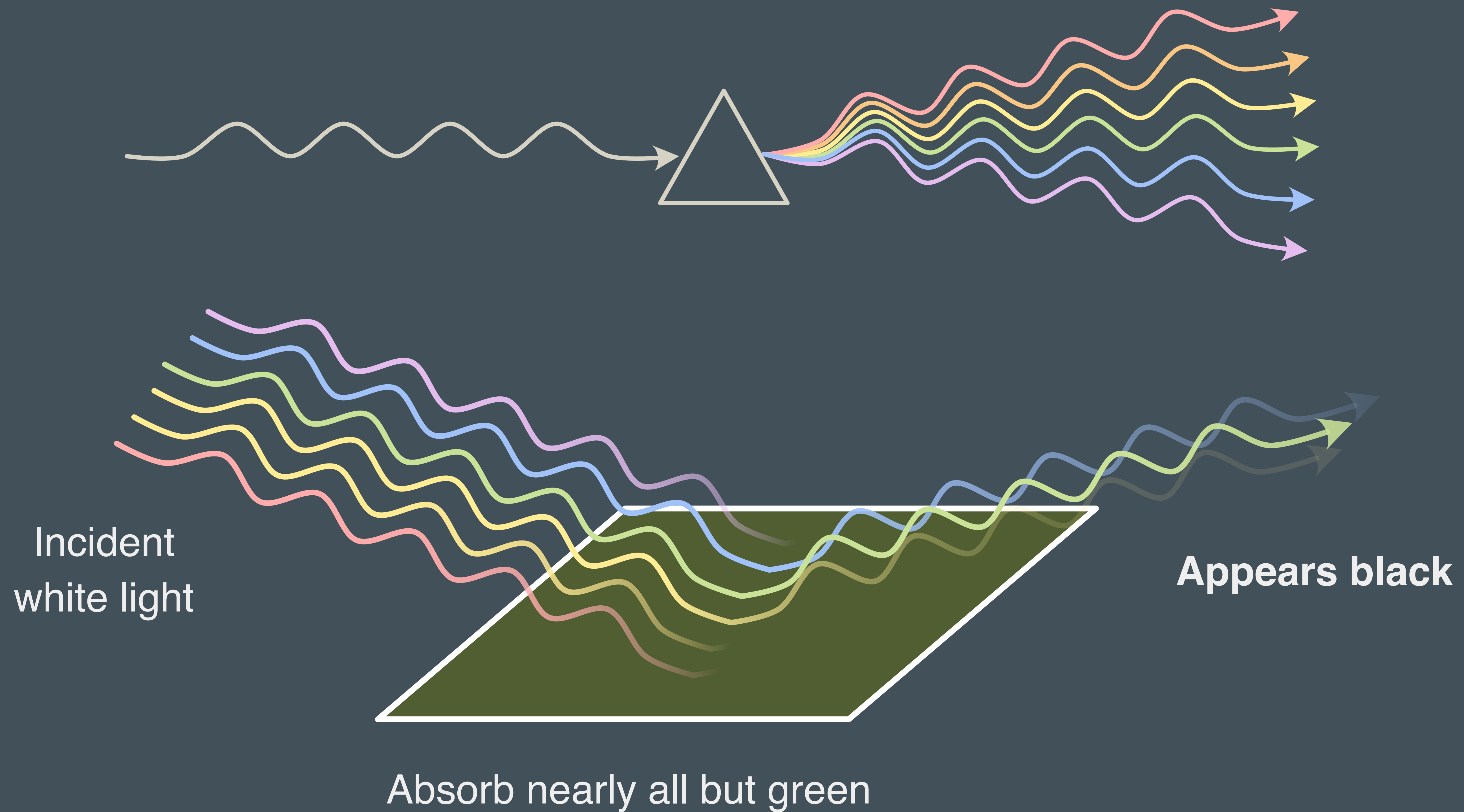
*NiO absorbs long and short wavelengths but absorbs a
bit less in the green region of the spectrum*
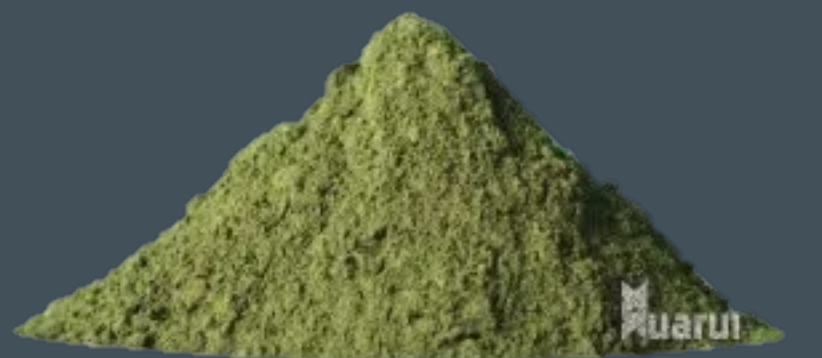
NiO

The color wheel
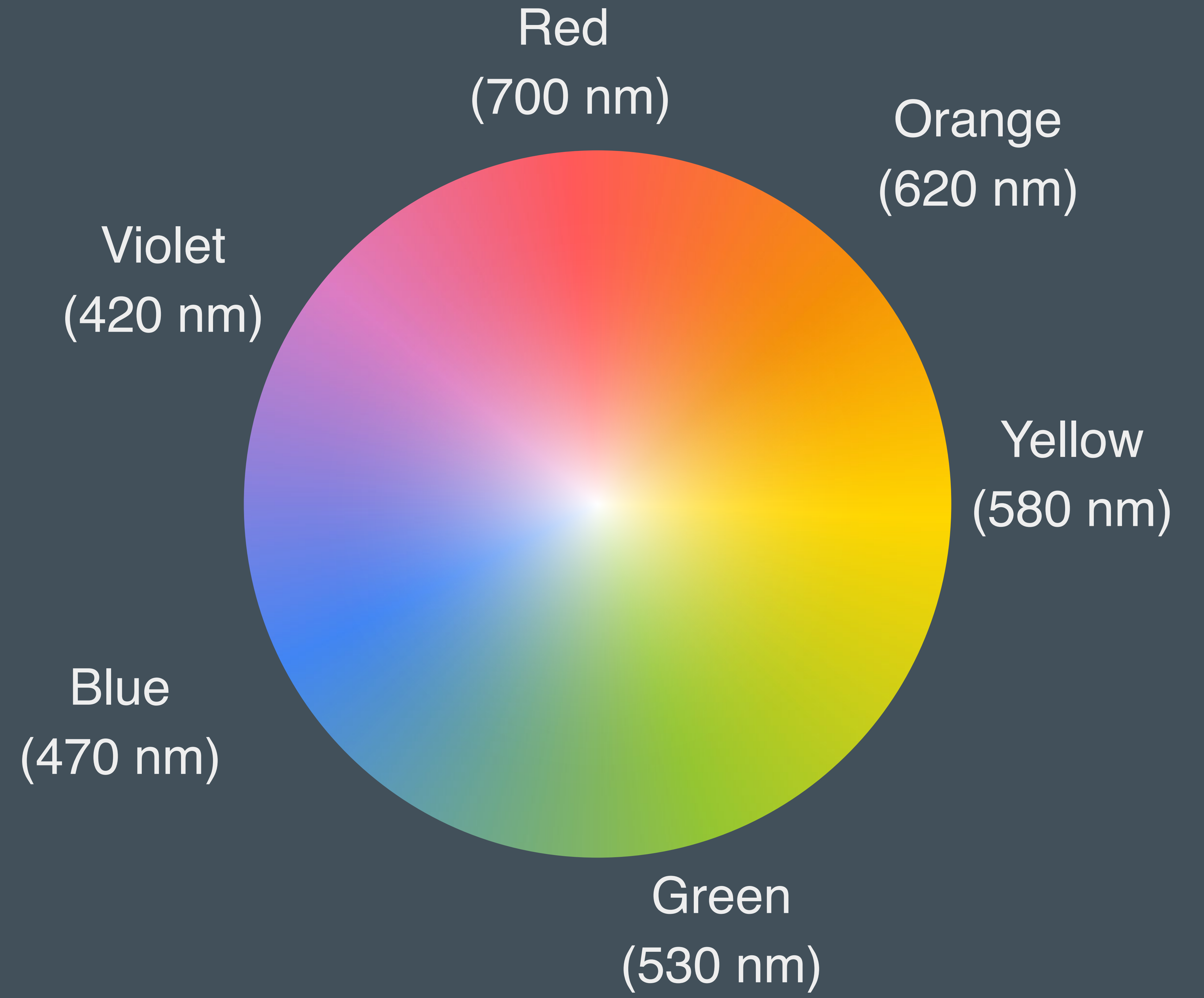
Example

If a sample absorbs light with a wavelength of 620 nm, what color is it?

Red
(700 nm)

Orange
(620 nm)

Violet
(420 nm)

Yellow
(580 nm)

Blue
(470 nm)

Green
(530 nm)

Colors of aqueous ions

Light passes through a transparent media (like a solution). Only colors that are not absorbed can pass through
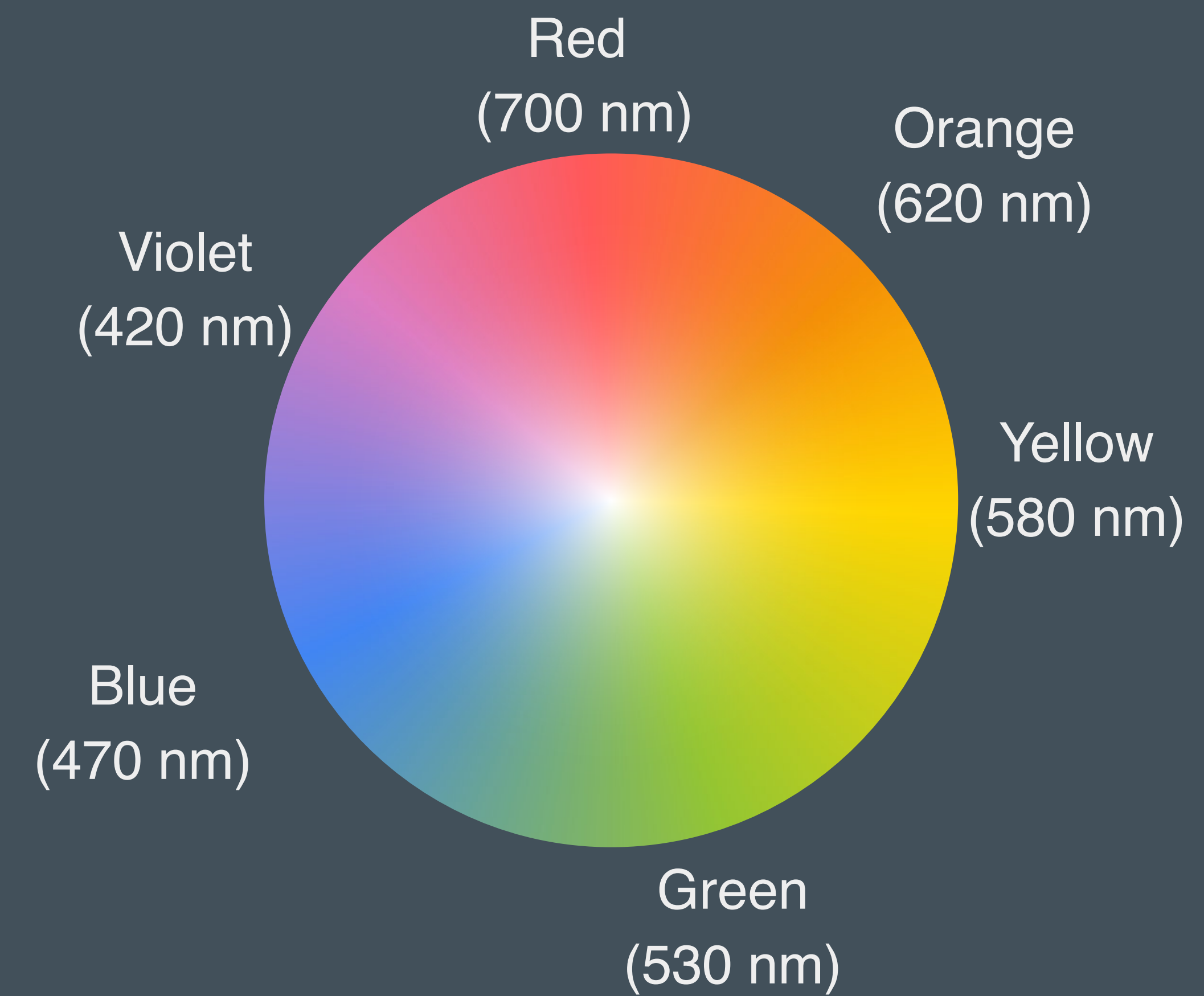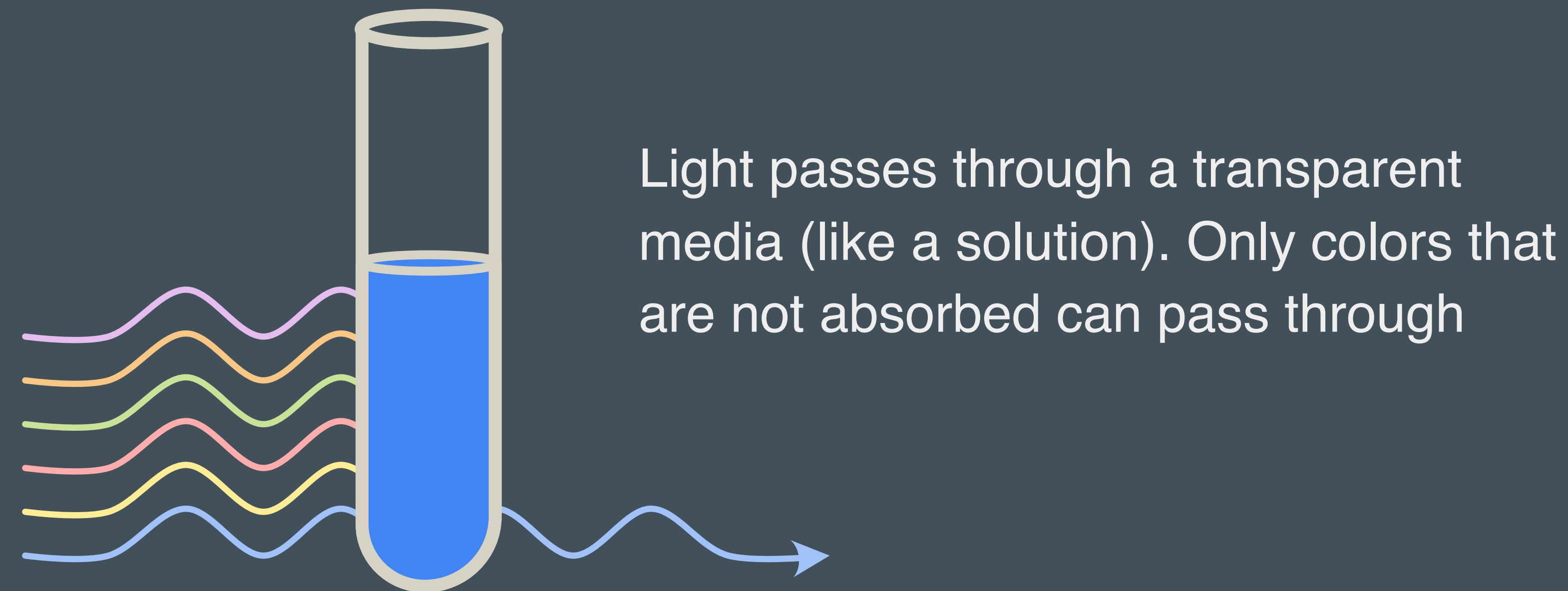
$$A = \epsilon \cdot c \cdot l$$

c = concentration (M)

l = path length (cm)

ϵ = molar absorptivity (M/cm)

A = Absorbance (unitless)

| 3+ | | 2+ | 3+ | 4+ | 5+ | | 2+ | 3+ | 6+ | | 2+ | 7+ | | 2+ | 3+ | | 2+ | | 2+ | | 2+ |
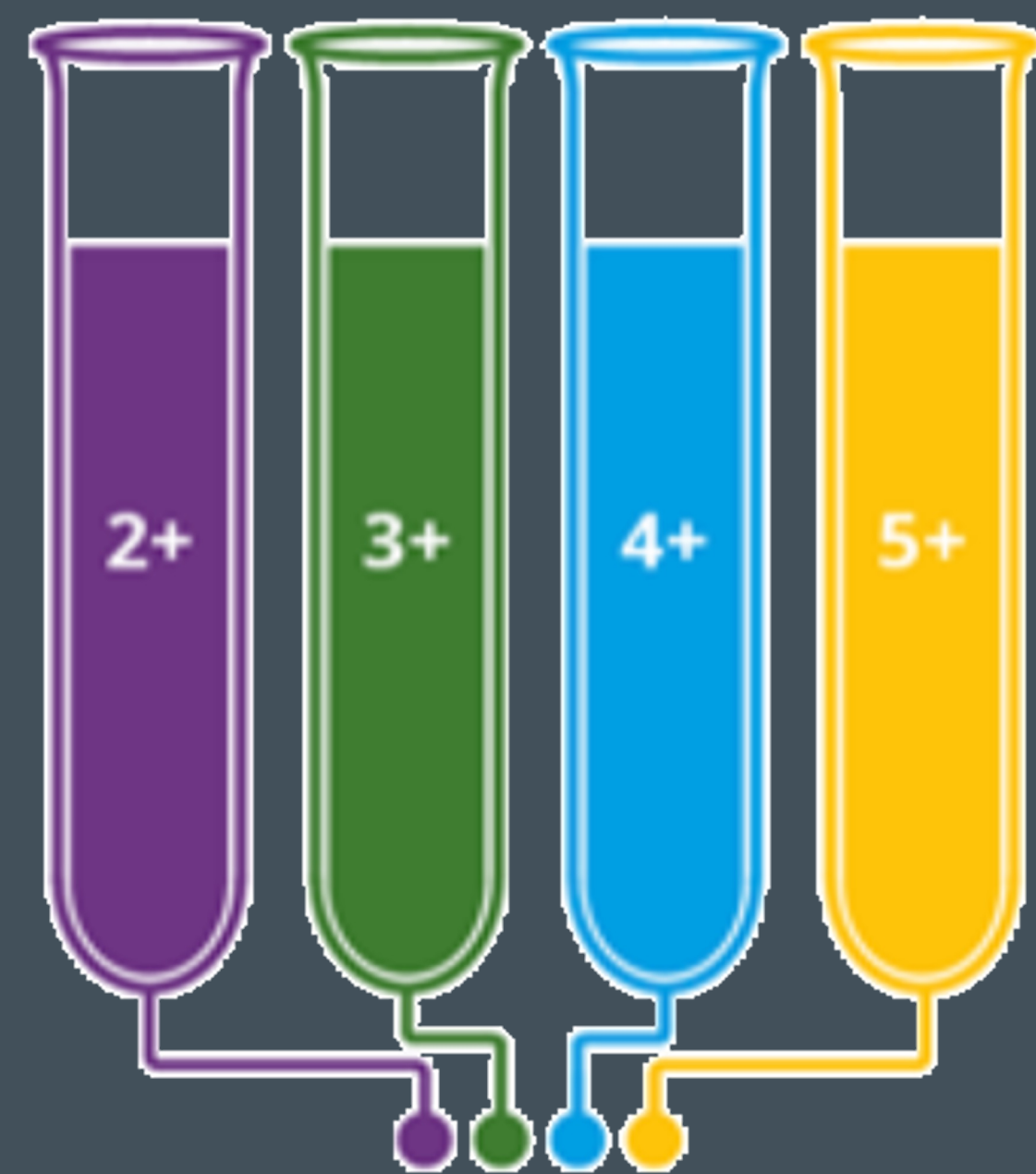
Ti   V   Cr   Mn   Fe   Co   Ni   Cu

In the Lab
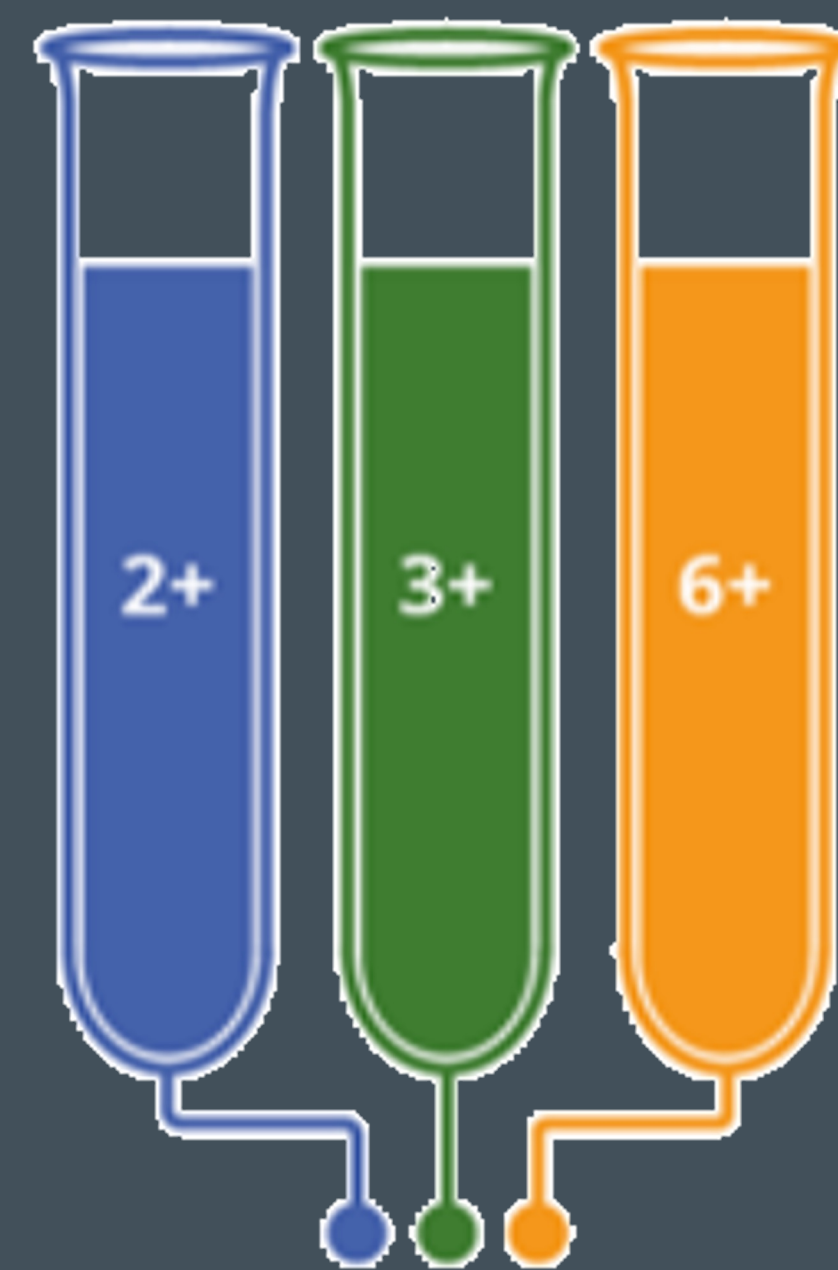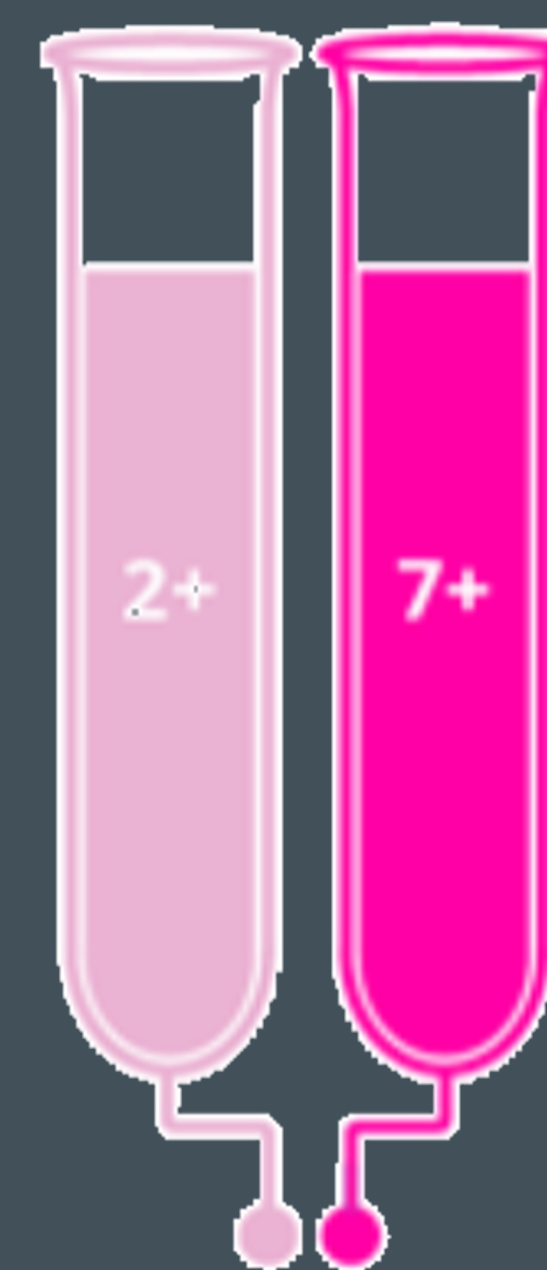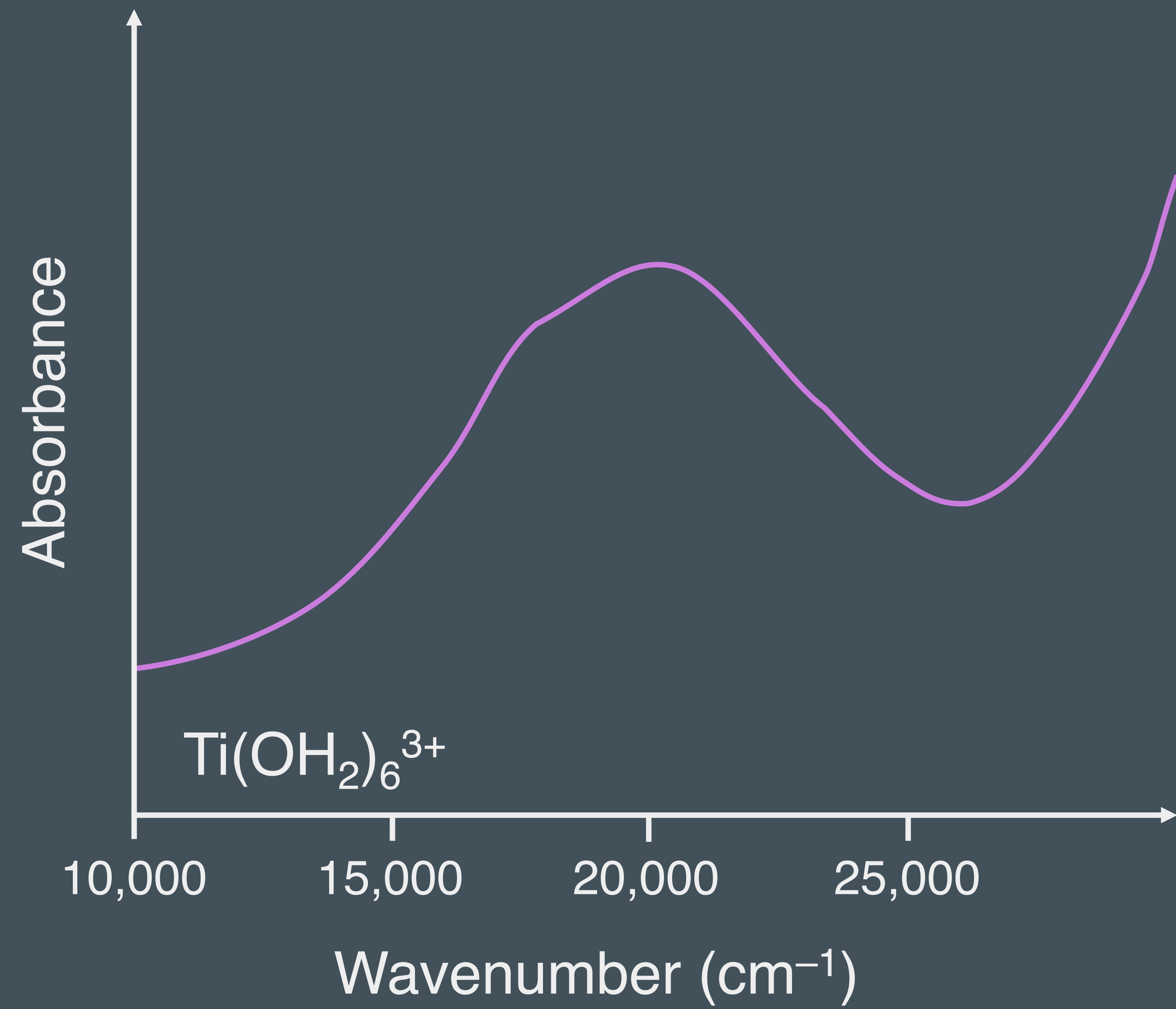
Absorbance vs Wavenumber (cm^{-1}) for Ti(OH$_2$)$_6$$^{3+}$

Measures of photons in chemistry

Photon Energy

Electron volt (eV): Kinetic energy by a single electron accelerated through a 1 V potential. 1 eV = 96.48 kJ/mol (1.602E–19 J)

Wavenumber (cm^{-1}): Antiquated unit often found in UV-vis spectroscopy and IR spectroscopy that is in proportion to the photon energy. ~8000 cm^{-1} = 1 eV (0.8% error)

Wavelength

Nanometers (nm): the distance between maxima in a coherent ray of monochromatic light. Spectrometers are built to measure/control wavelength directly. Wavelength is a unit of *measurement* but a poor unit for *analysis*. $hc = 1240\ eV \cdot nm$ (0.01% error)

Absorptions

Absorptions arise when electrons move from a lower energy level to a higher energy level.

Common Examples:

- Transitions between metal-centered orbitals possessing *d*-character (*d-d* transitions)

- Transitions between metal and ligand centered MOs which transfer charge from metal to ligand or ligand to metal

Absorption Patterns

There are a few common patterns:

1. d^1, d^4, d^6, and d^9 complexes consist of one broad absorption

2. d^2, d^3, d^7, and d^8 complexes consist of three broad absorptions

3. d^5 complexes consist of a series of very weak, relatively sharp absorptions

Charge Transfer Complexes

A **charge transfer complex** is one in which a donor and acceptor interact *weakly* together with some transfer of electronic charge, usually facilitated by the acceptor.

In metal complexes, intense absorptions (typically in the UV or visible part of the electronic spectrum) may arise from ligand-centered $n - \pi^*$ *or* $\pi - \pi^*$ transitions, or from the transfer of electric charge between ligand and metal orbitals.

Charge Transfers

The transfer of electric charge between ligand and metal orbitals can happen in two ways:

Ligand-to-Metal Charge Transfer, LMCT: transfer of an electron from an orbital with primarily ligand character to one with primarily metal character

Metal-to-Ligand Charge Transfer, MLCT: transfer of an electron from an orbital with primarily metal character to one with primarily ligand character

Example

Select all of the following that are true for a typical LMCT.

a. Metal oxidation

b. Metal reduction

c. Ligand oxidation

d. Ligand reduction

LMCT

In the below series, the LMCT band moves to shorter wavelength (higher energy) as the metal center's becomes harder to reduce.

$[MnO_4]^-$	528 nm
$[TcO_4]^-$	286 nm
$[ReO_4]^-$	227 nm

LMCT

In the below series, the LMCT band moves to longer wavelength (lower energy) as the ligand becomes easier to oxidize.

$[FeCl_4]^{2-}$	220 nm
$[FeBr_4]^{2-}$	244 nm

MLCT

MLCT typically occurs when the ligand has a vacant, low-lying π^* orbital.

The associated absorption often occurs in the UV region of the spectrum and is not commonly responsible for producing intensely colored species.

Selection rules for photon absorption/emission

Electronic transitions between energy levels obey the following selection rules:

1. Spin Selection Rule: $\Delta S = 0$

Transitions may occur from singlet to singlet or from triplet-to-triplet states, but a change in spin multiplicity is **forbidden**.

Selection rules for photon absorption/emission

2. Laporte Selection Rule: $\Delta l = \pm 1$

There must be a change in parity.

- Less strict compared to the spin rule
- Strict wrt $\Delta l = \pm 1$
- Easily *relaxed* by removing inversion symmetry from from the molecular geometry

Allowed transitions:

$$g \leftrightarrow u$$

$$s \rightarrow p, \, p \rightarrow d, \text{ and } d \rightarrow f$$

Forbidden transitions:

$$g \leftrightarrow g \text{ and } u \leftrightarrow u$$

$$s \rightarrow s, \, p \rightarrow p, \, d \rightarrow d, \text{ and } f \rightarrow f$$

$$s \rightarrow d \text{ and } p \rightarrow f$$

Exceptions

A spin-forbidden transition becomes "allowed" if a change in spin multiplicity occurs.

This is only possible due to spin-orbit coupling and **vibronic coupling**.

Vibronic coupling occurs when molecular vibrations cause a symmetrical molecule to temporarily lose it's symmetry. At this moment, mixing between *p* and *d* orbitals can occur.

Example

In general, which complexes are more intensely colored?

A. Octahedral

B. Tetrahedral

Example

True/False: A transition from a t_{2g} to an e_g orbital in the complex $[V(OH_2)_6]^{3+}$ is both spin and Laporte forbidden.

In the Lab

Type of Transition	Typical ε_{max} (L mol^{-1} cm^{-1})
Spin-forbidden '*d–d*'	<1
Laporte-forbidden but spin-allowed '*d–d*'	1–10 (centrosymmetric) 10–1000 (non-centrosymmetric)
Charge Transfer (fully allowed)	1000–50,000