ChemE 2200 – Applied Quantum Chemistry Lecture 8

Today:

The Interaction of Electromagnetic Radiation with Matter: The Fates of Electronic Excited States, continued.

Defining Question:

What is the mechanism of blacklight posters? How do posters absorb UV photons and emit visible photons?

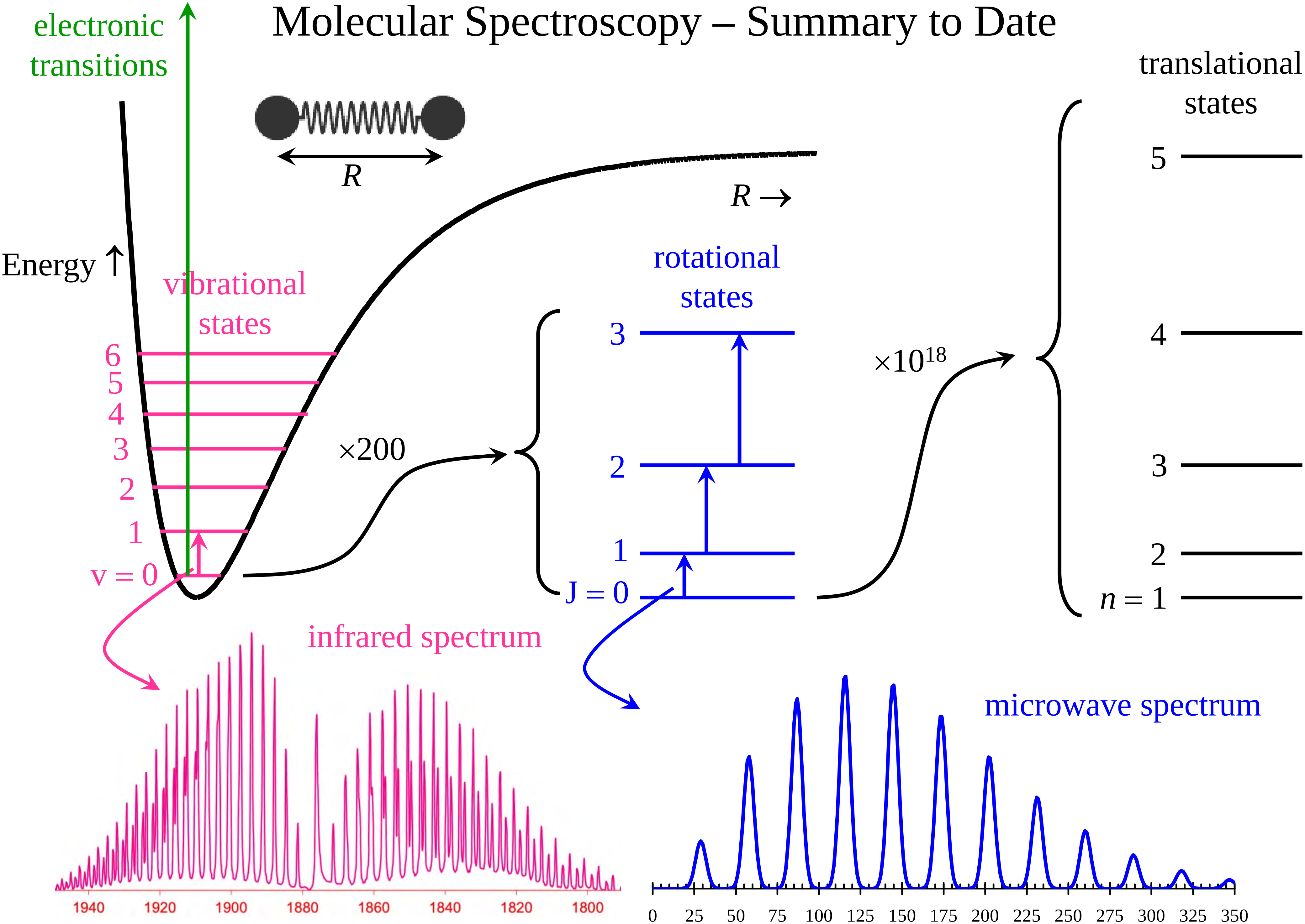
Reading for Today's Lecture:

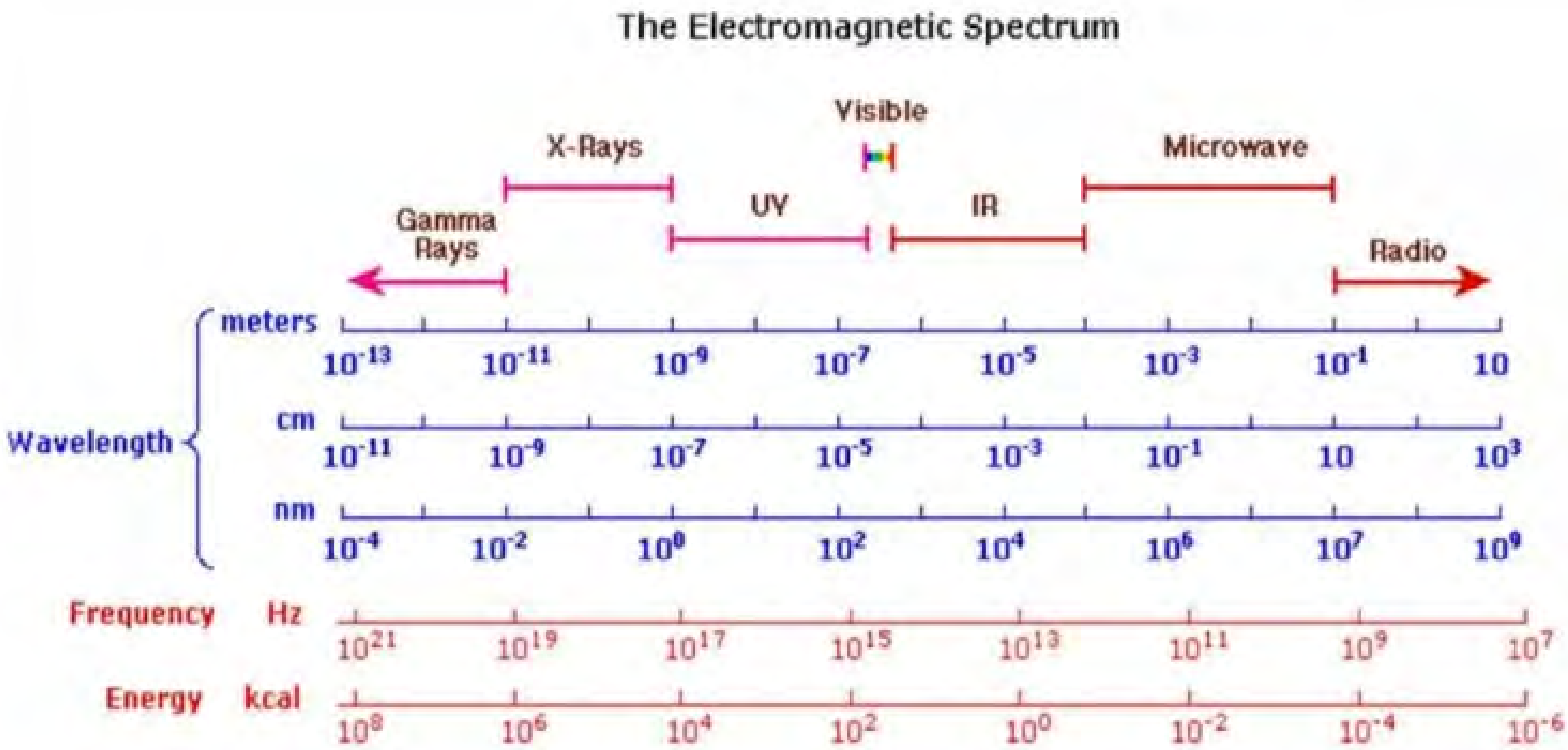
McQuarrie & Simon, 13.6, 13.7.

Reading for Quantum Lecture 9:

Electrons in Solids Handout: pp 1-10.

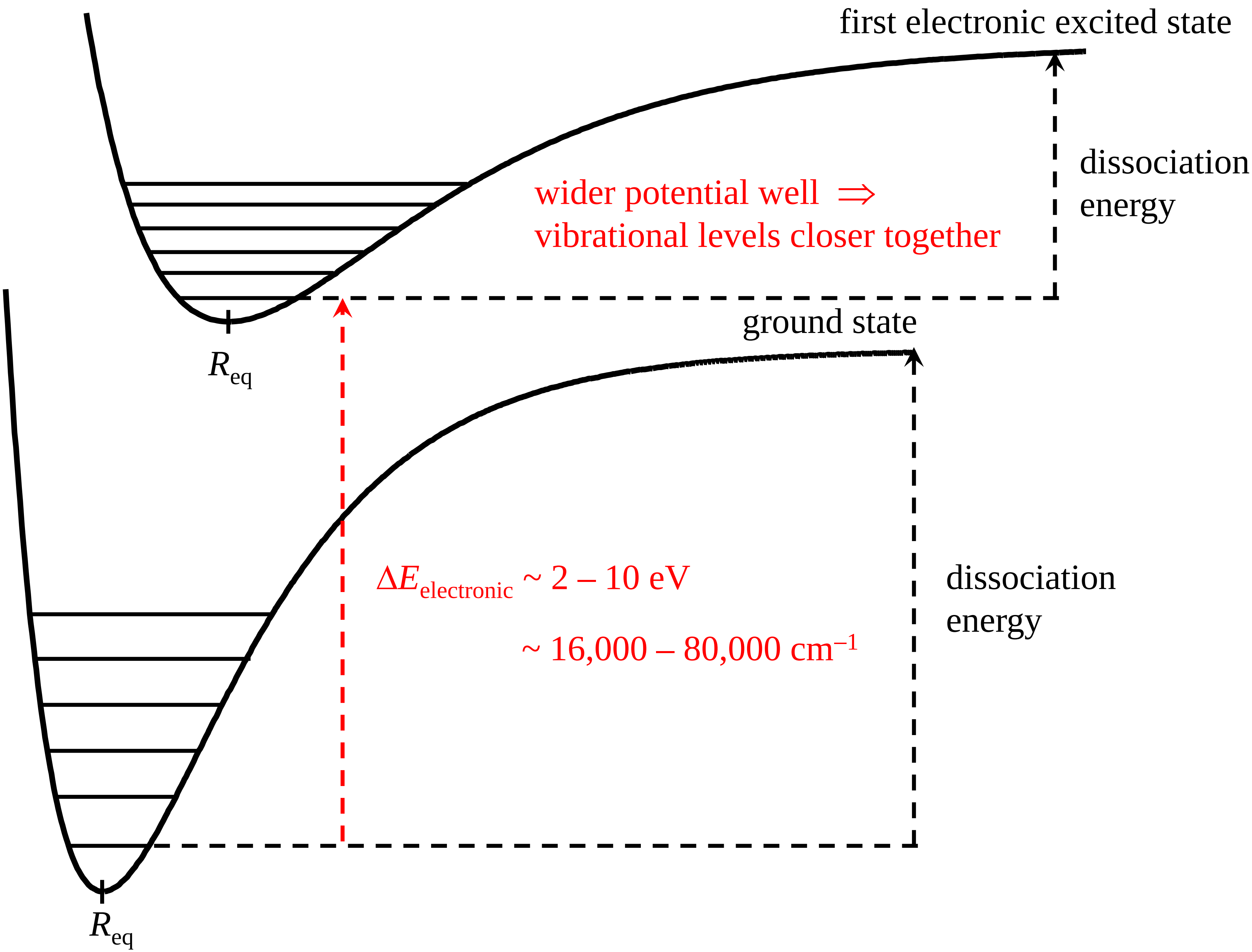
Molecular Spectroscopy – Summary to Date



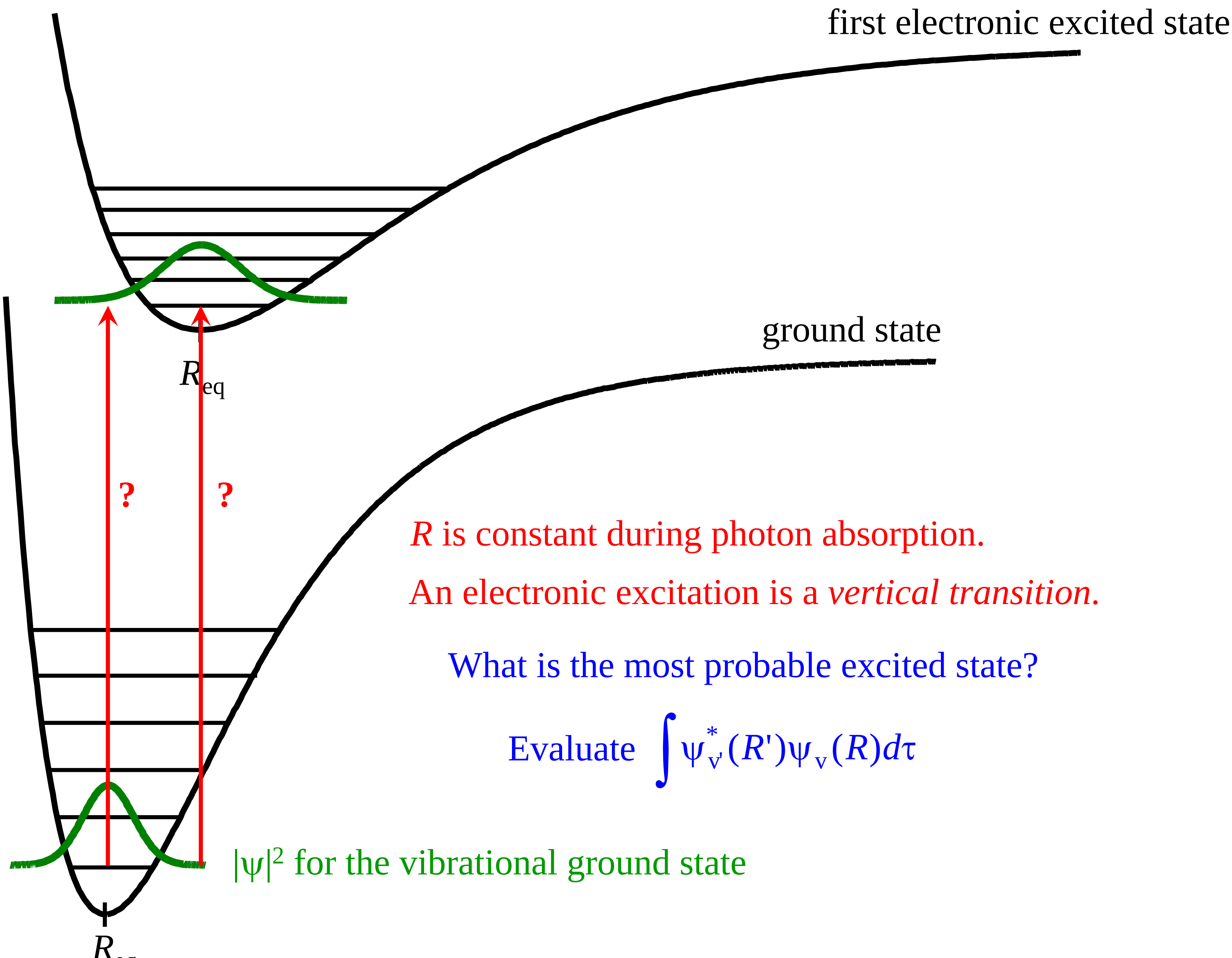


From ‘spectroscopy’ lecture by Ayesha Shafi

Recap: Electronic Ground State and First Excited State



Recap: Electronic Transitions



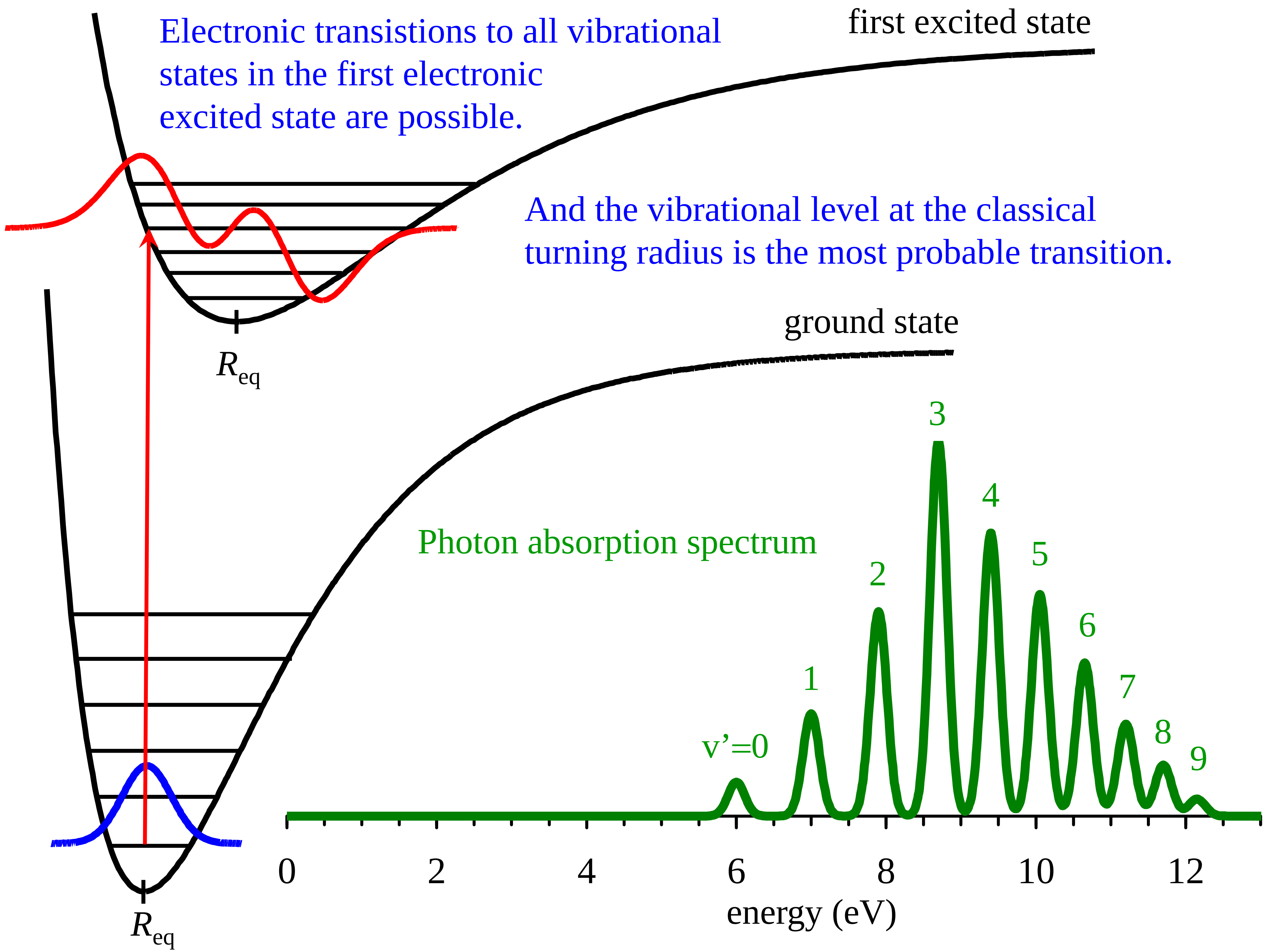
R is constant during photon absorption.

An electronic excitation is a *vertical transition*.

What is the most probable excited state?

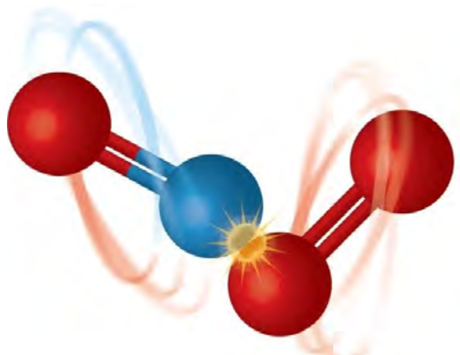
Evaluate $\int \psi^*_{v'}(R')\psi_v(R)d\tau$

Recap: Electronic Transitions – Photon Absorption Spectrum



Recap: Fates of Electronic-Vibrational Excited States

1. Chemical Reaction – molecule dissociates
2. Radiative Decay – molecule emits a photon
3. Non-Radiative Decay – molecule transfers energy to other gas molecules by collisions



Which fate is more likely?

transition	EM band	ΔE	ν_{photon}	collision rate*	spontaneous emission rate**
electronic	UV/visible	10-30 eV	$\sim 10^{15}$/sec	$\sim 10^{10}$/sec	$\sim 10^{8}$/sec
vibrational	infrared	~0.3 eV	$\sim 10^{13}$/sec	$\sim 10^{10}$/sec	$\sim 10^{2}$/sec
rotational	microwave	~0.001 eV	$\sim 10^{11}$/sec	$\sim 10^{10}$/sec	$\sim 10^{-4}$/sec

*CO at 300K and 1 atm

**spontaneous emission rate $\propto \nu^3$

collision rate > spontaneous emission rate

All excited states decay by collisions?

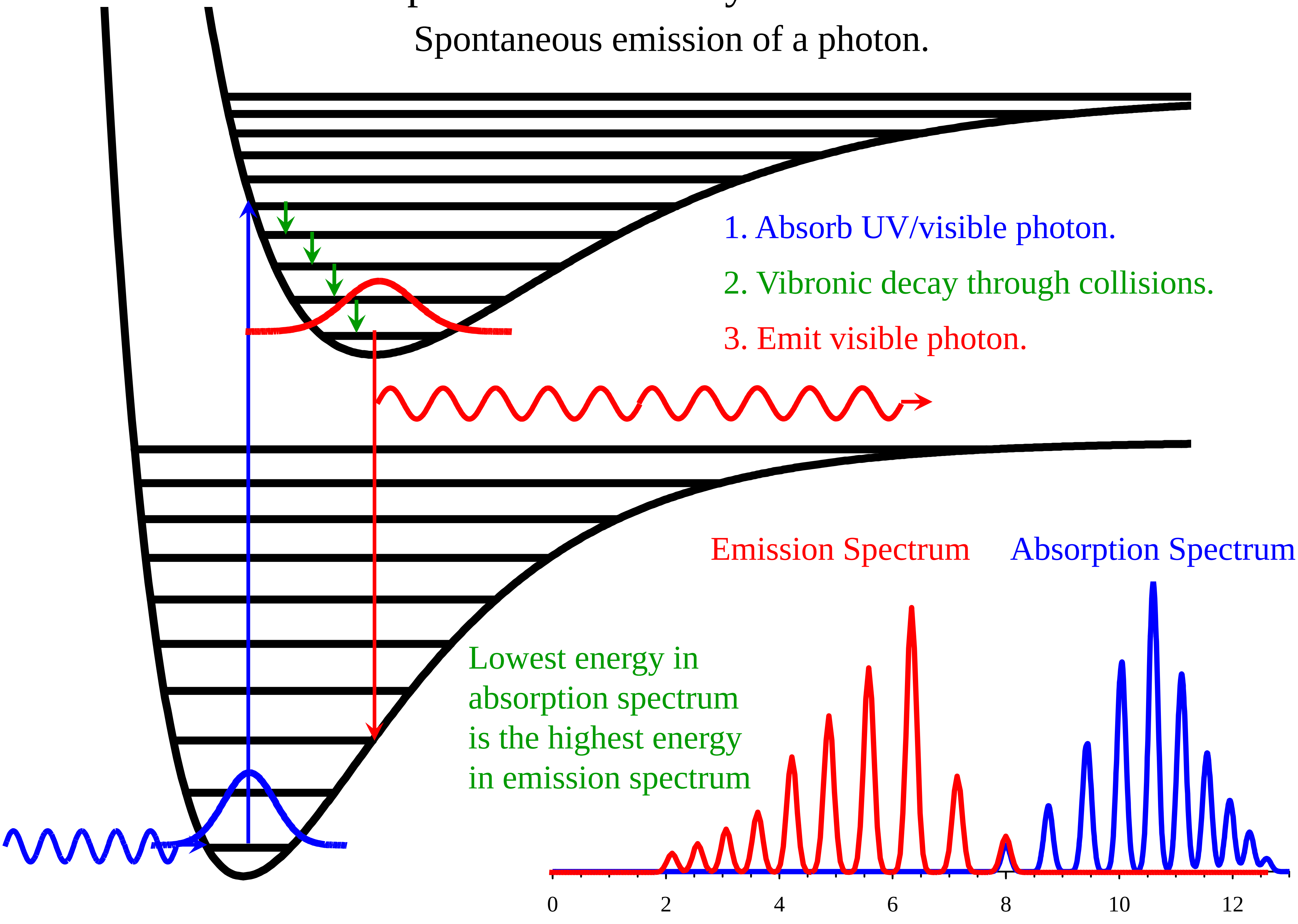
No – collision energy << electronic energy.

Typical K.E. at 300 K = 0.025 eV. ($\langle v \rangle$ = 475 m/sec for CO)

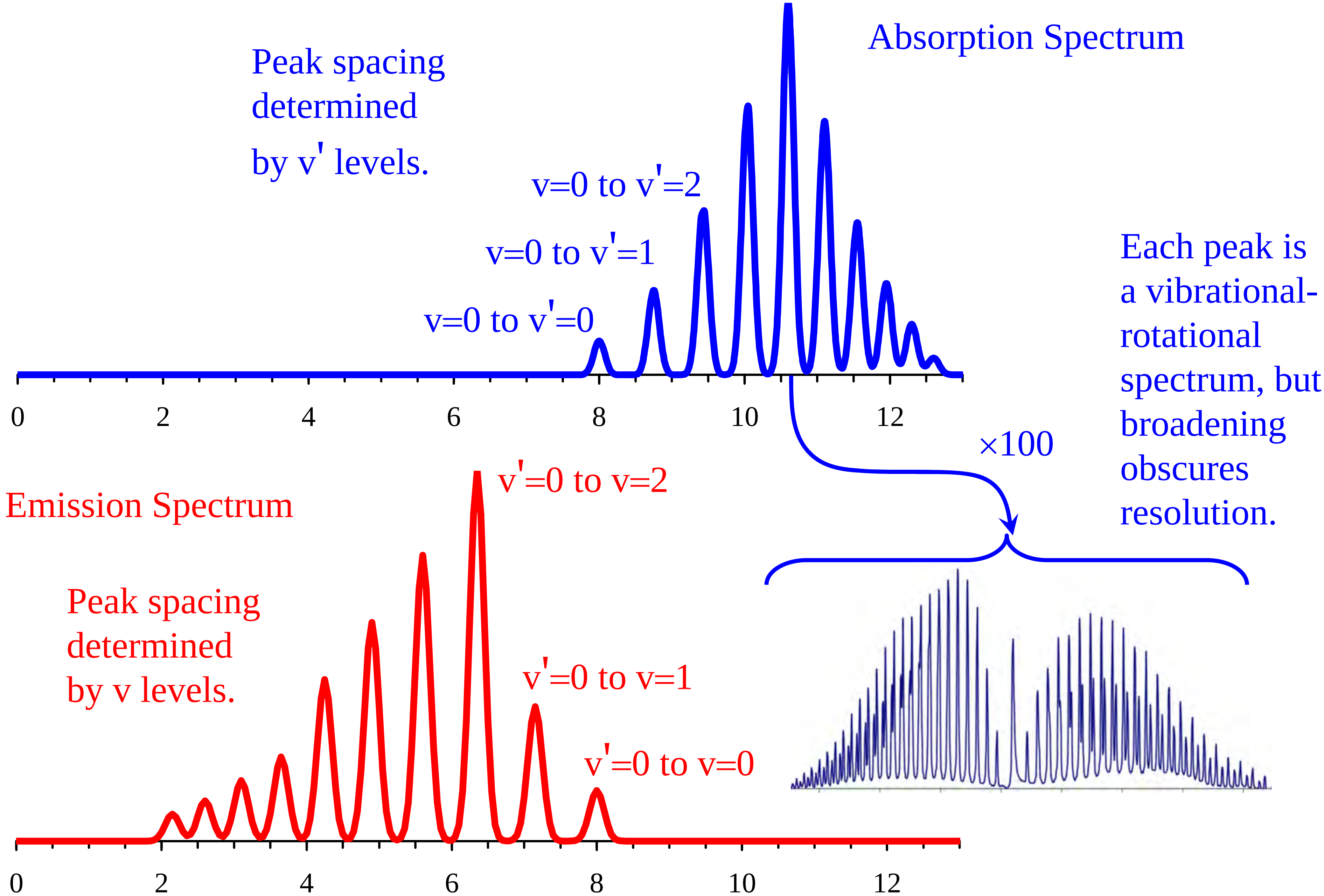
Image from G. Graziano, *Molecular collisions: A crash course in energy transfer*. Nature Review Chemistry 2, 0127 (2018)

Recap: Radiative Decay - Fluorescence

Spontaneous emission of a photon.

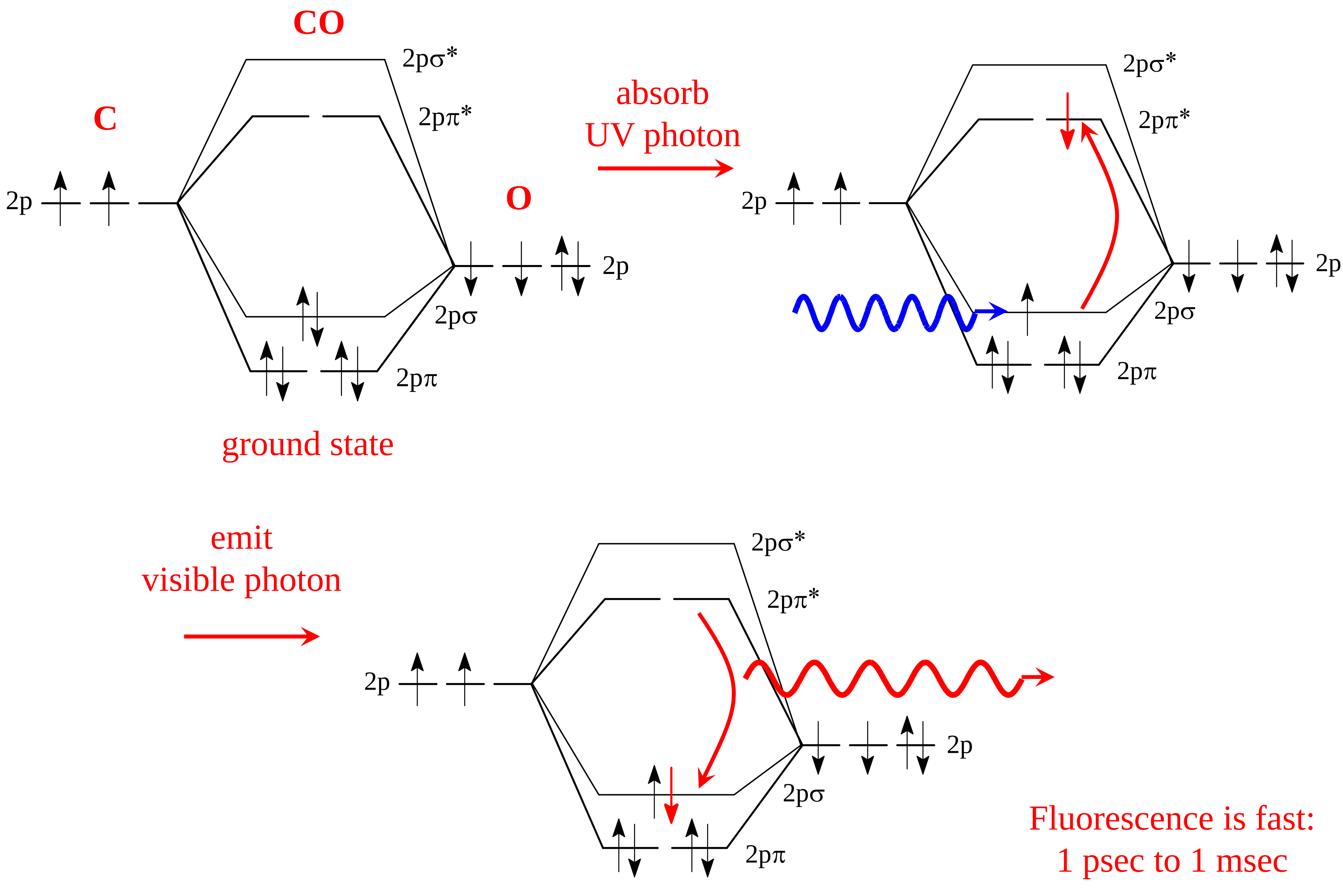


Recap: Radiative Decay - Fluorescence

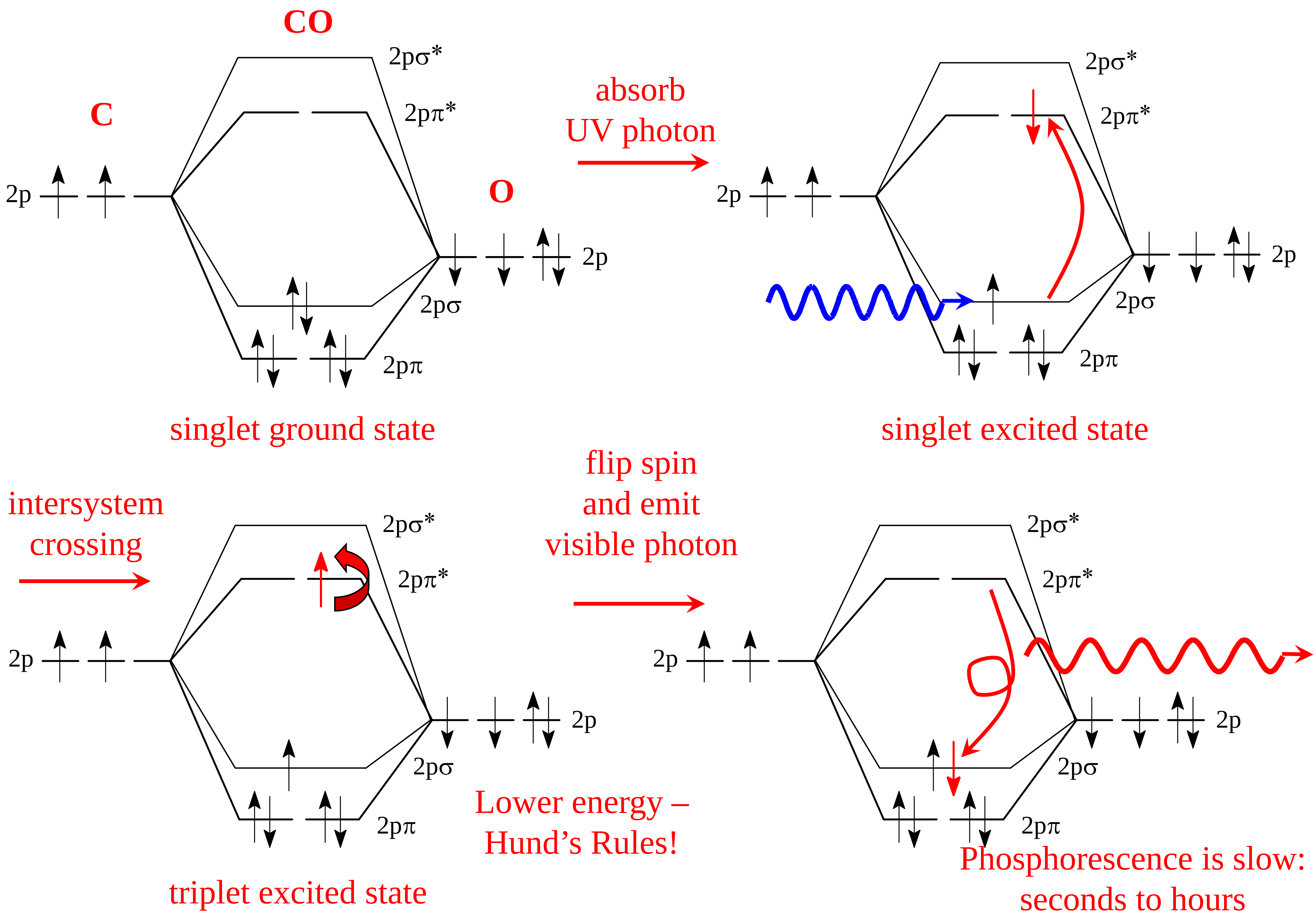


Fluorescence: absorb UV photon, emit visible photon. Fast process: 1 ps to 1 ms.

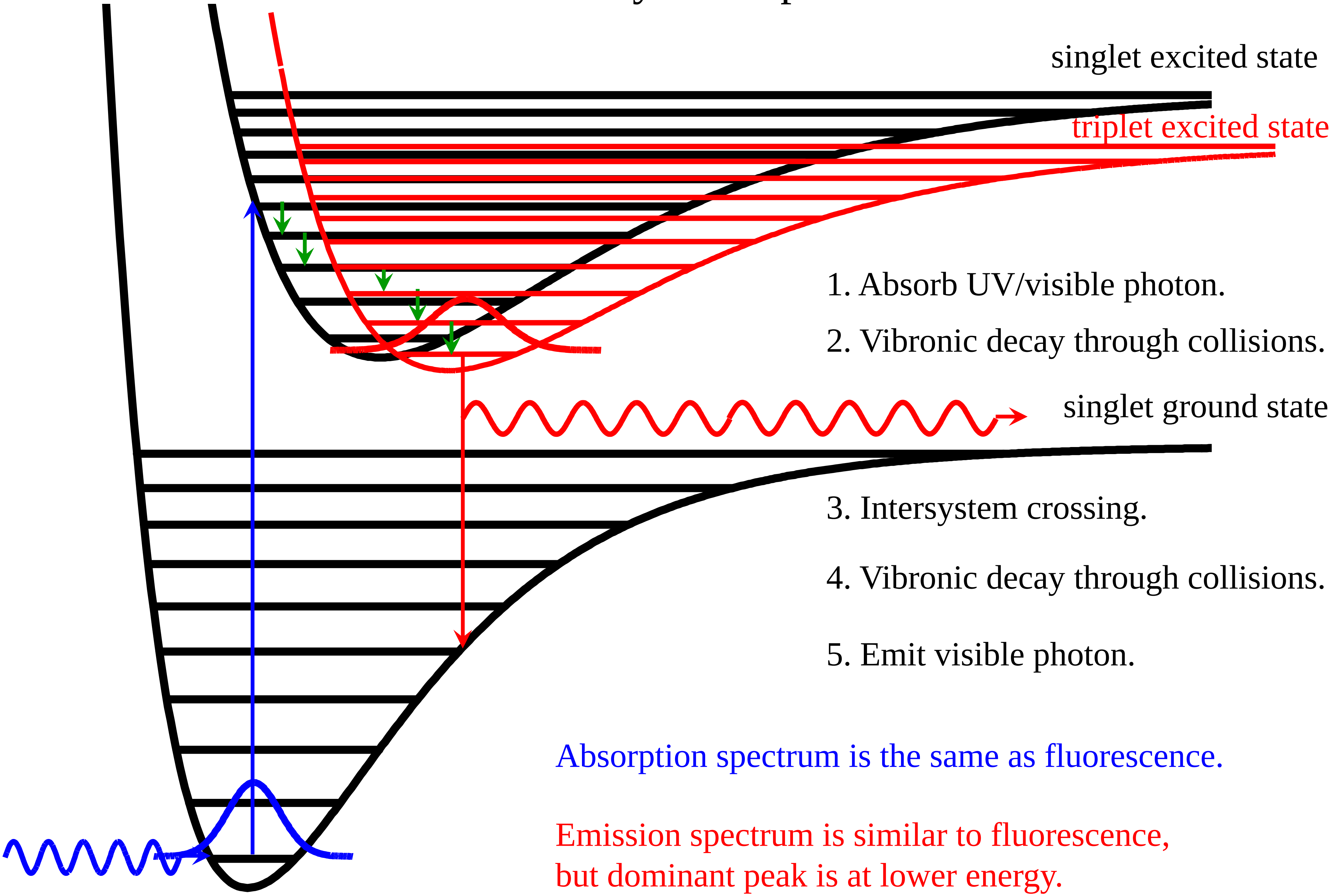
Fluorescence – Molecular Orbital Energy Levels



Phosphorescence – Molecular Orbital Energy Levels



Radiative Decay - Phosphorescence



1. Absorb UV/visible photon.
2. Vibronic decay through collisions.
3. Intersystem crossing.
4. Vibronic decay through collisions.
5. Emit visible photon.

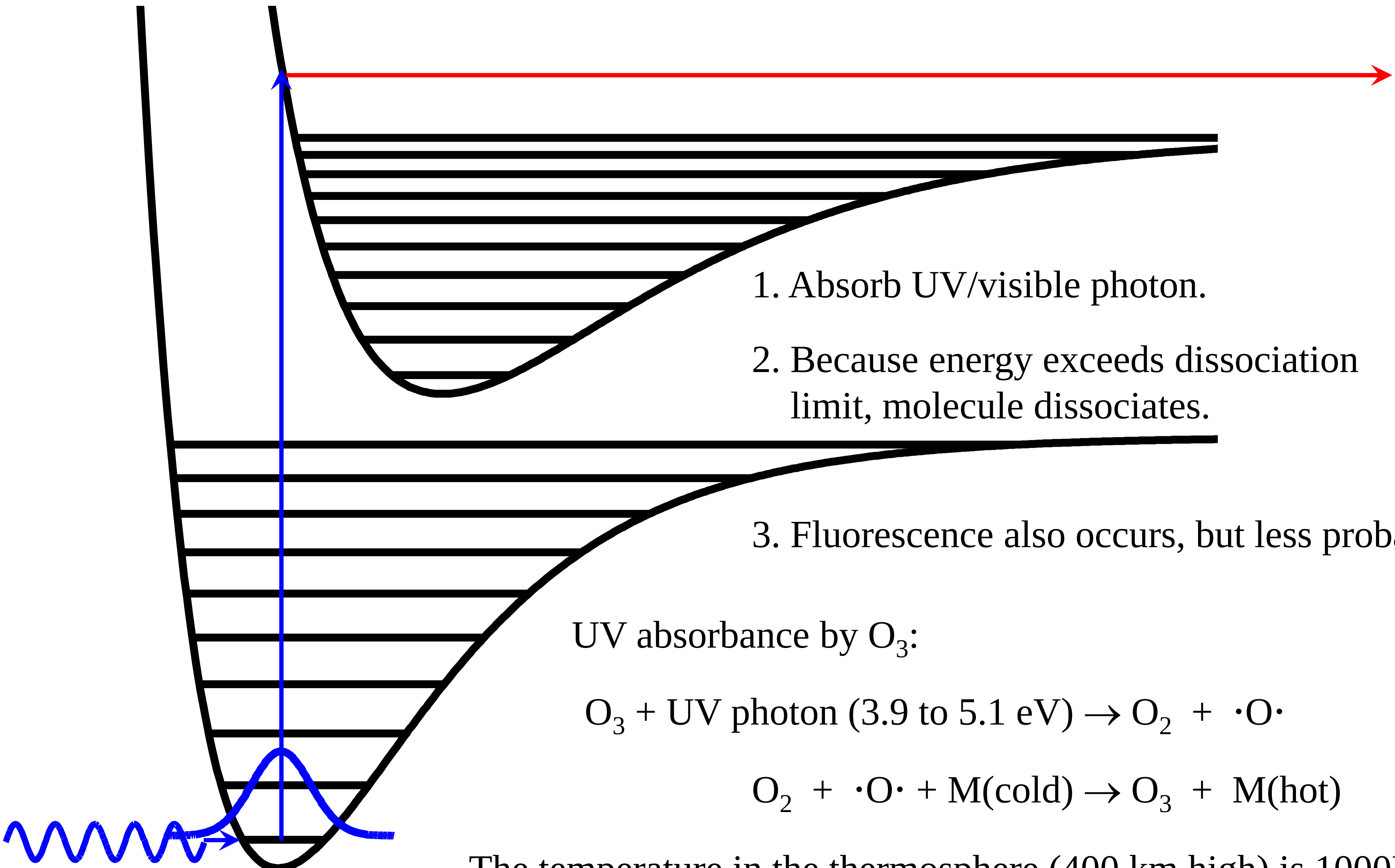
Absorption spectrum is the same as fluorescence.

Emission spectrum is similar to fluorescence, but dominant peak is at lower energy.

Photon-Induced Dissociation

Allowed for most molecules, but it is rare.

For some molecules, the first electronic excited state is shifted to a longer $R_{equilibrium}$.



1. Absorb UV/visible photon.
2. Because energy exceeds dissociation limit, molecule dissociates.
3. Fluorescence also occurs, but less probable.

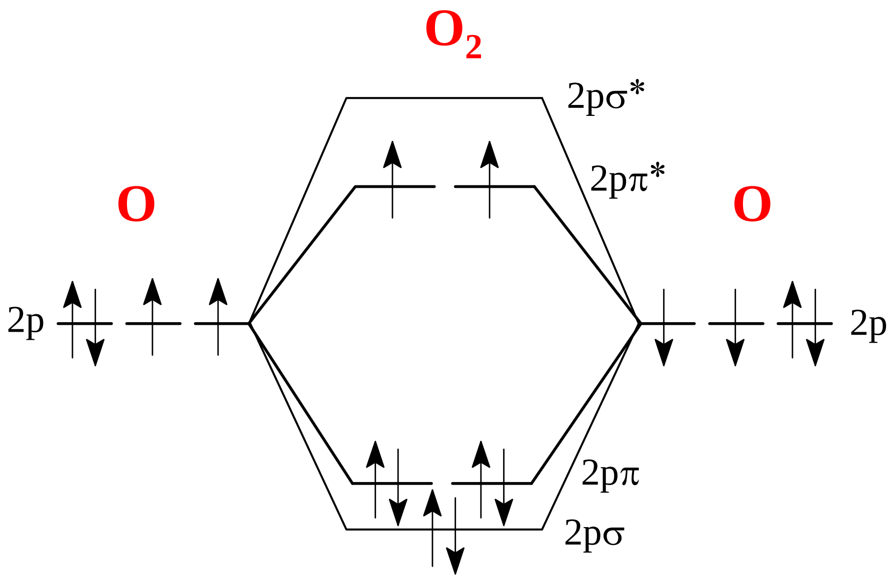
UV absorbance by O_3:

O_3 + UV photon (3.9 to 5.1 eV) → O_2 + ·O·

O_2 + ·O· + M(cold) → O_3 + M(hot)

The temperature in the thermosphere (400 km high) is 1000K.

Photon-Induced Dissociation by Pre-Dissociation

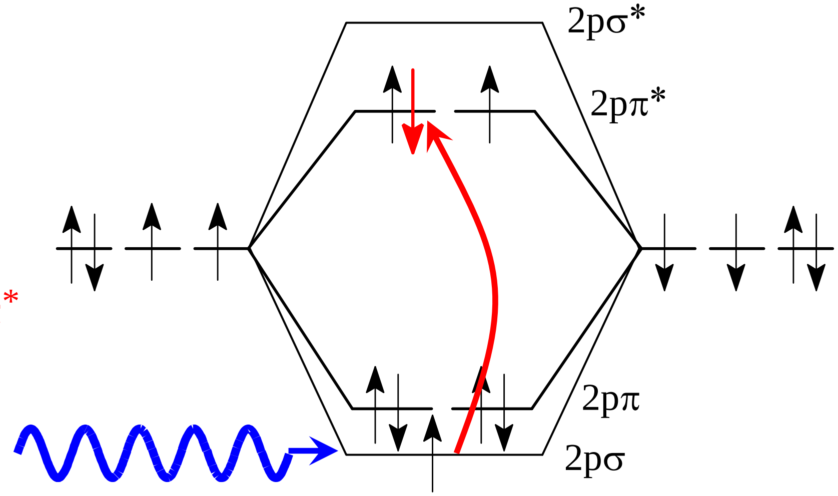


triplet ground state (Hund's Rule)

bond order = ½(6 – 2) = 2

absorb
UV photon

$2p_z\sigma \rightarrow 2p_x\pi^*$



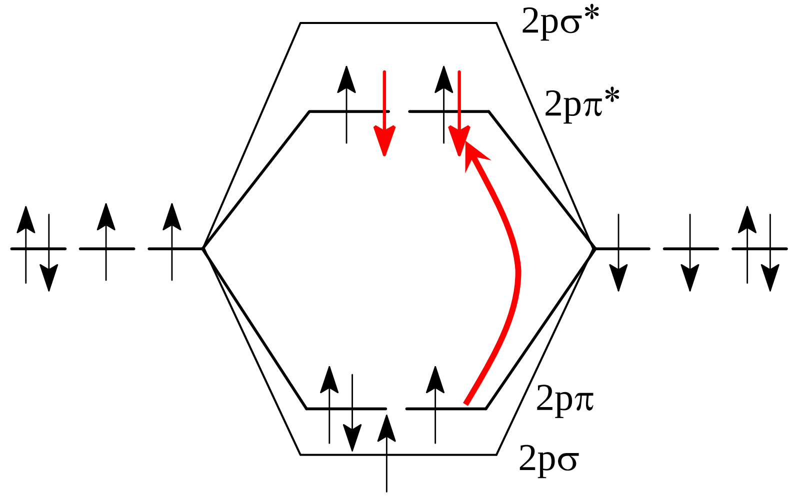
triplet excited state

bond order = ½(5 – 3) = 1

vibrational energy →
electronic energy

energy-level cross-over to
a non-bonded state

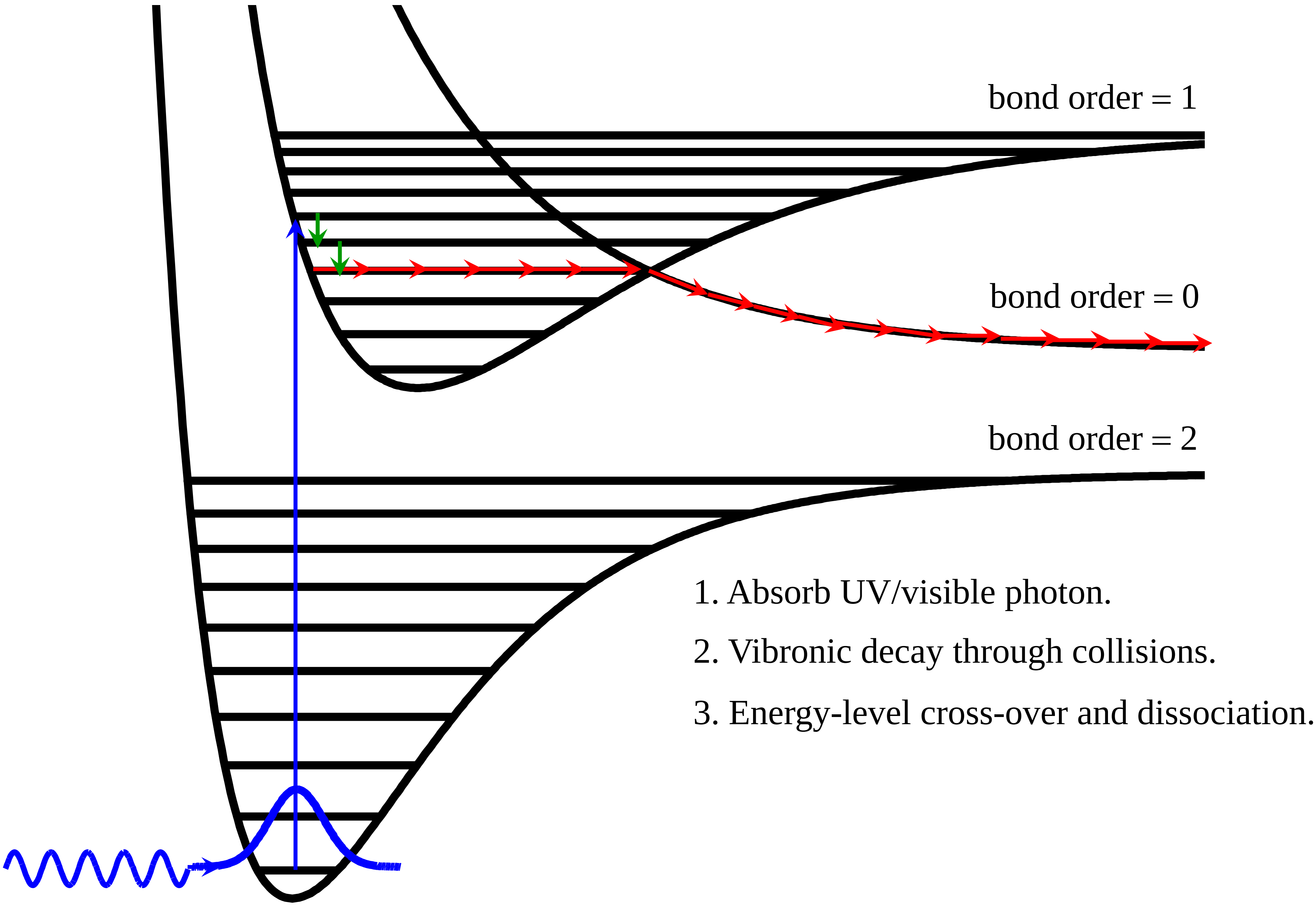
$2p_x\pi \rightarrow 2p_x\pi^*$



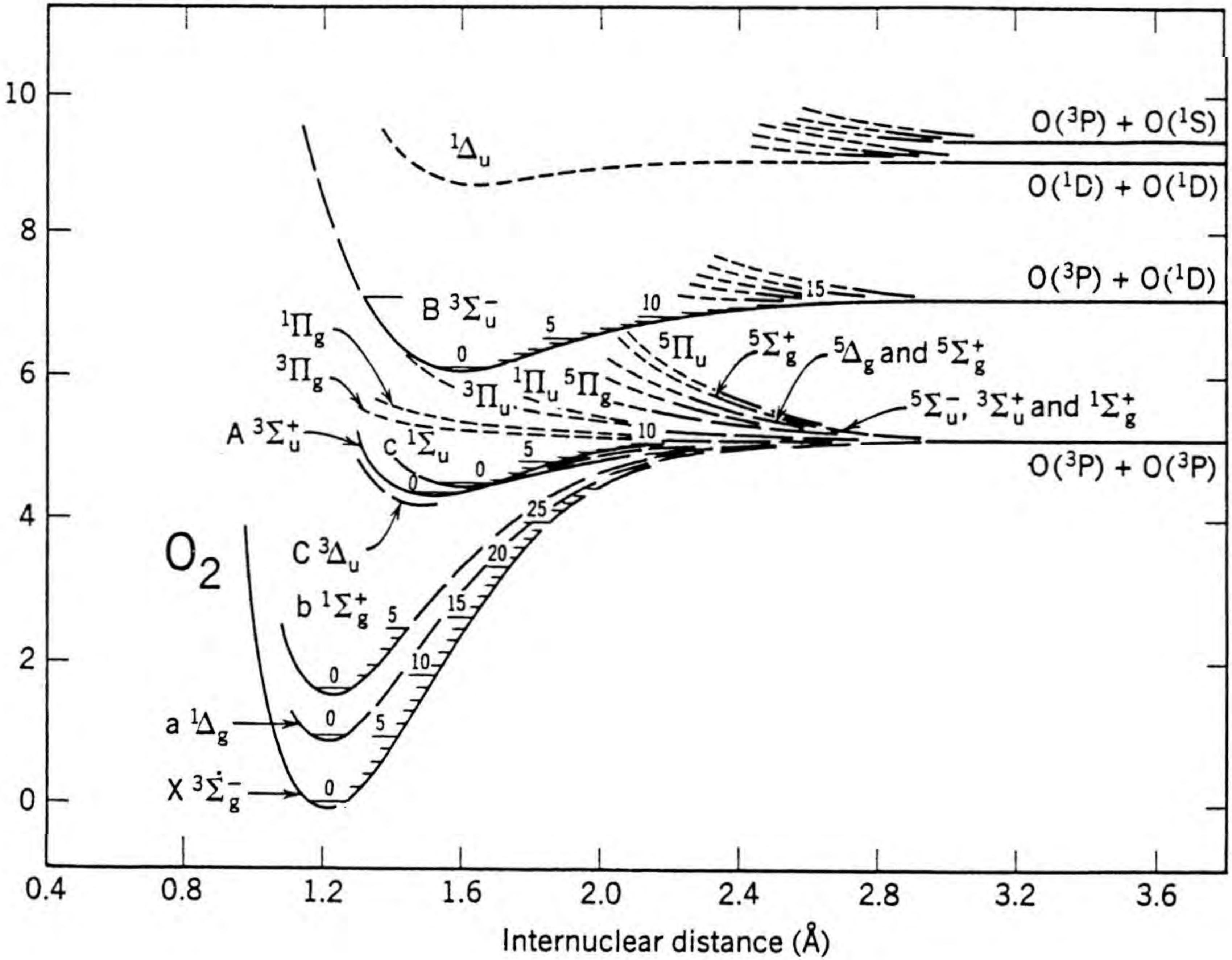
triplet excited state

bond order = ½(4 – 4) = 0

Photon-Induced Dissociation by Pre-Dissociation



Photon-Induced Dissociation by Pre-Dissociation: O_2



What causes the Space Shuttle ‘Halo’?

Shuttle velocity
= 25,000 mph
= 11,000 m/sec

$P = 10^{-12}$ atm

Mostly N_2 and O_2.

Molecular mean free path = 10^4 m

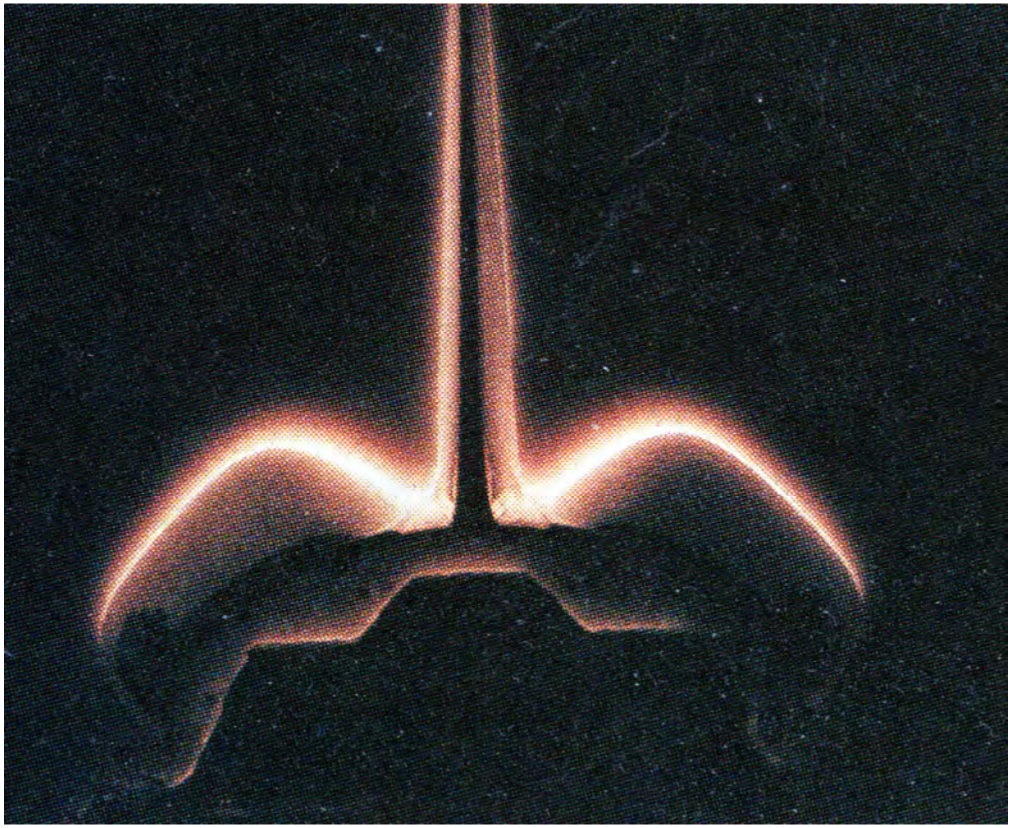
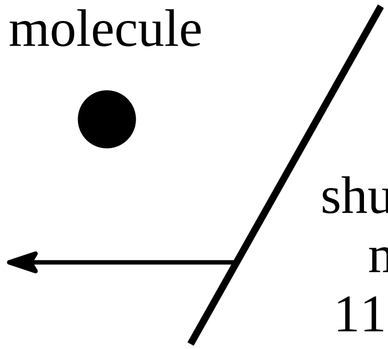


Image from *Chemical & Engineering News*, March 28, 1994.



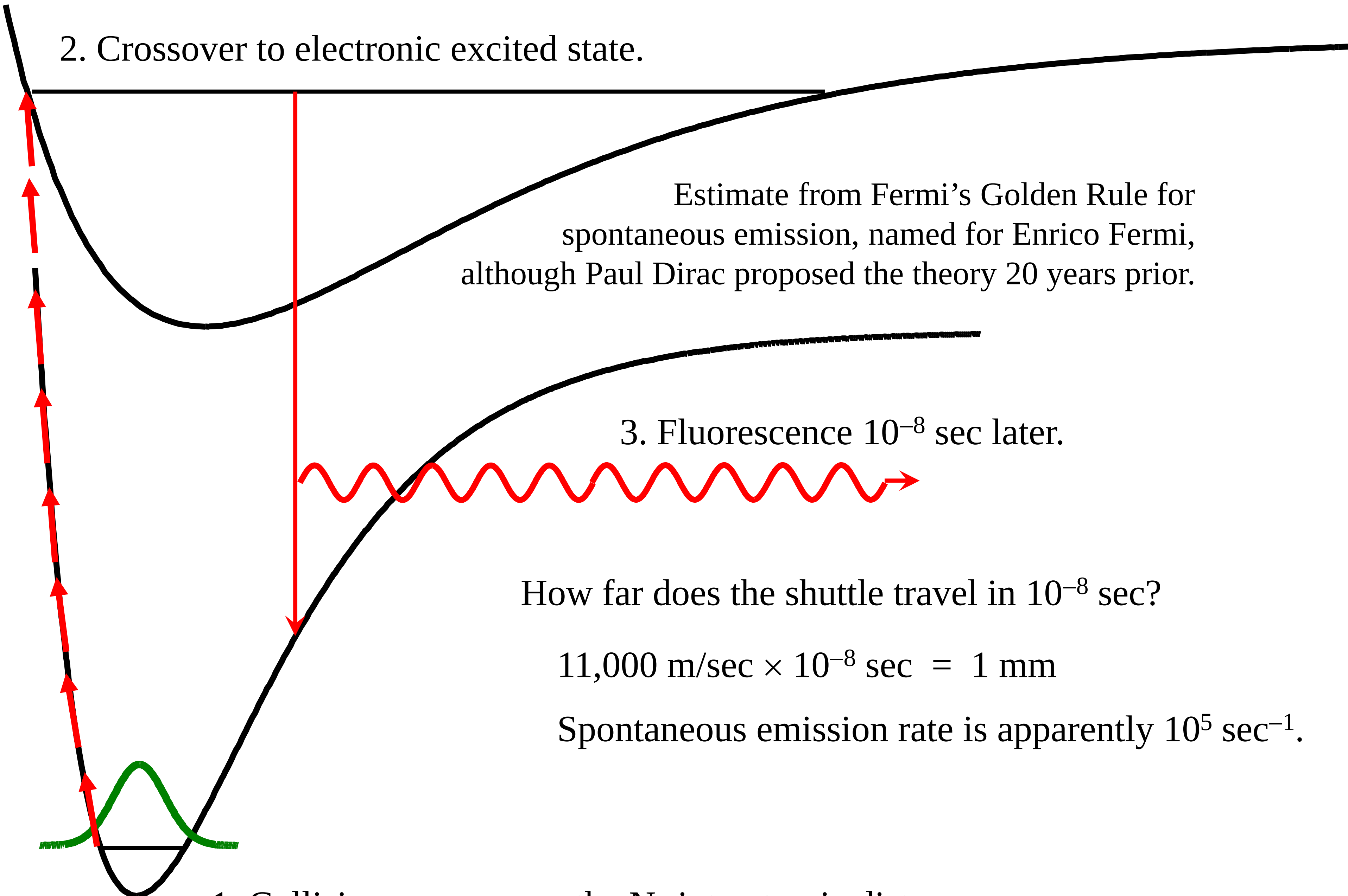
If the collision is elastic, what is the kinetic energy of the deflected molecule?

$$\text{K.E.} = \tfrac{1}{2}mv^2$$

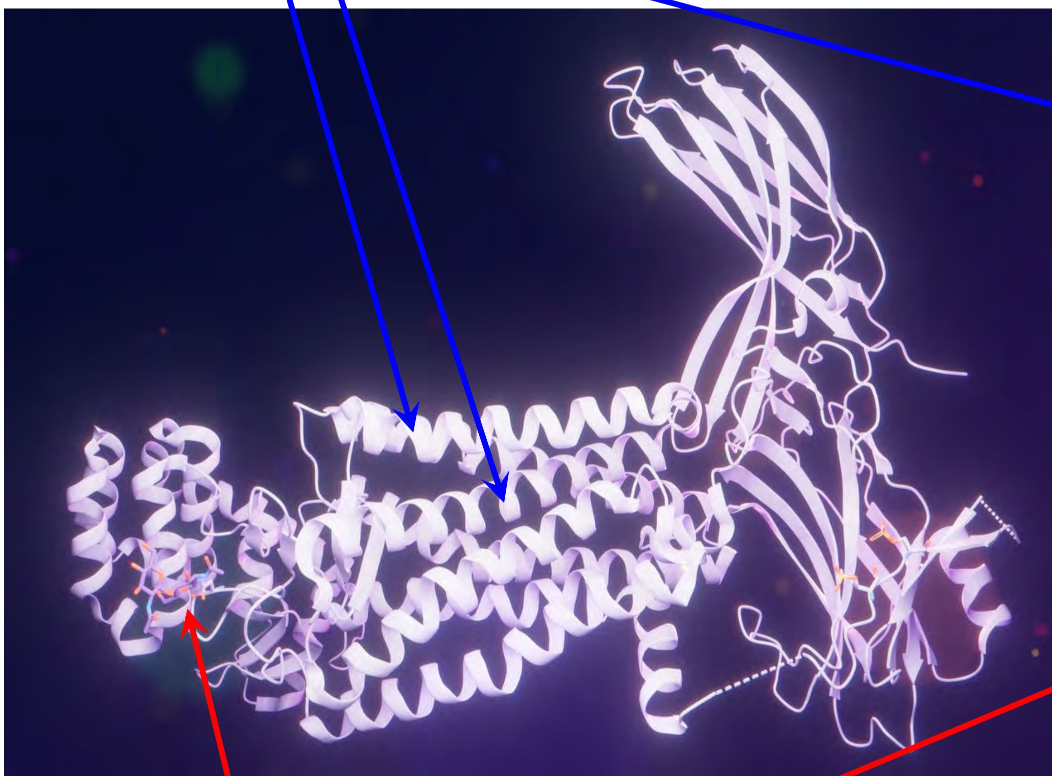
$$= \frac{\tfrac{1}{2}(28\,\text{amu})(1.7\times10^{-27}\ \text{kg/amu})(1.1\times10^{4}\ \text{m/sec})^2}{1.6\times10^{-19}\ \text{J/eV}}$$

$= 15$ eV UV/visible range (visible ≈ 4 eV)

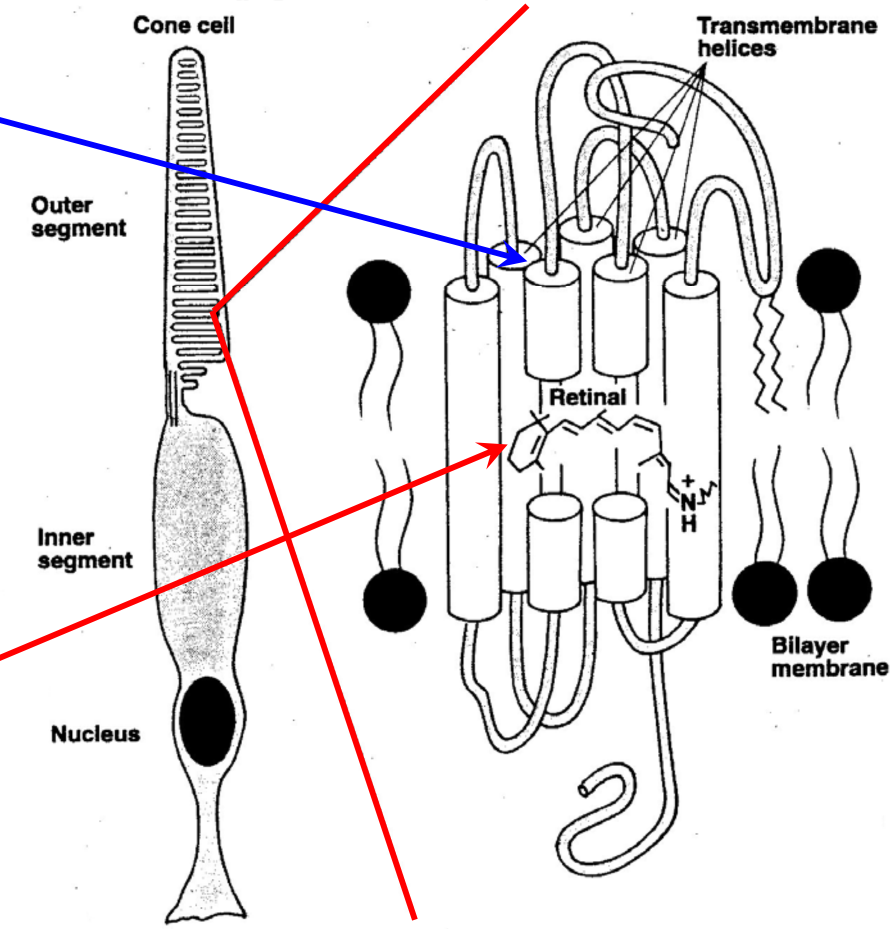
What causes the Space Shuttle ‘Halo’?



Harvesting Visible Photons: Vision and Rhodopsin

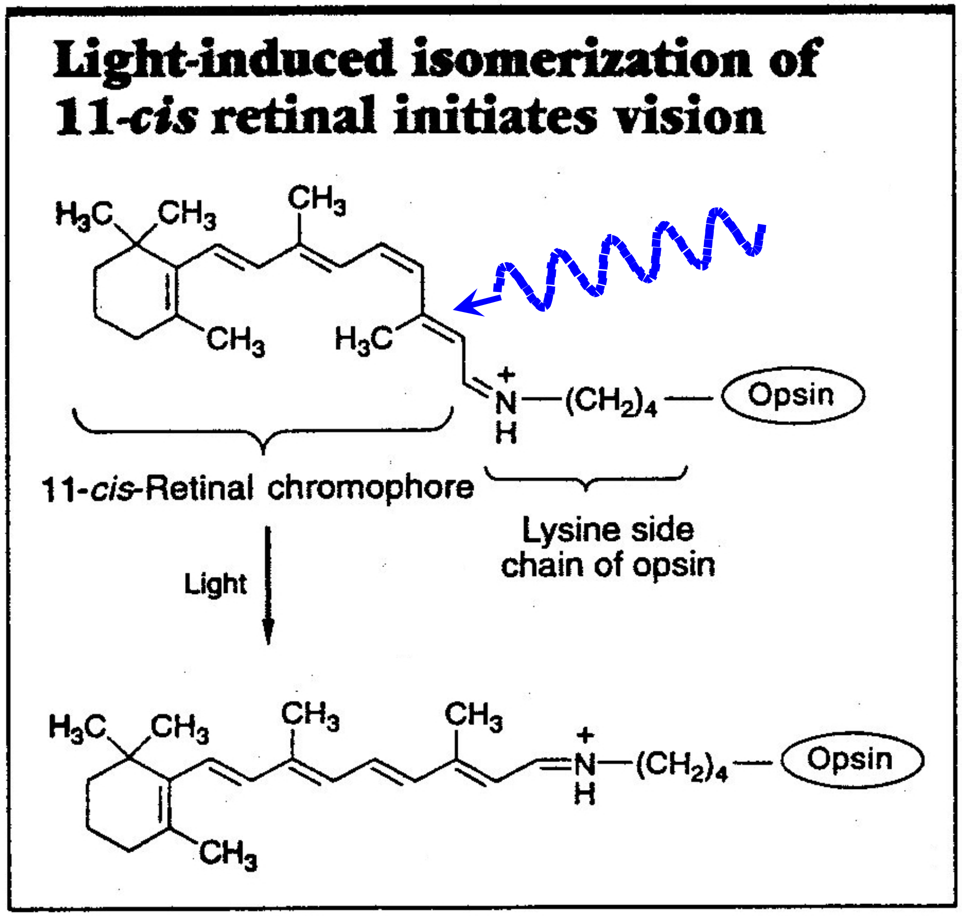


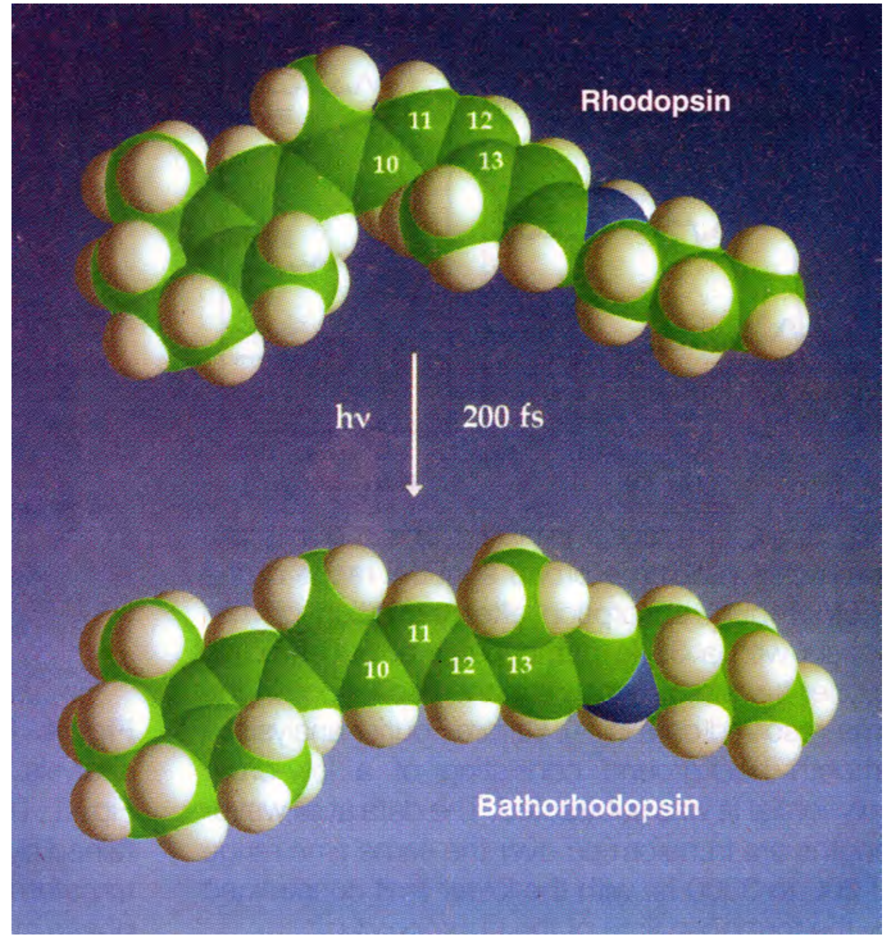
Interaction of 11-*cis* retinal with transmembrane helices affects pigment absorption



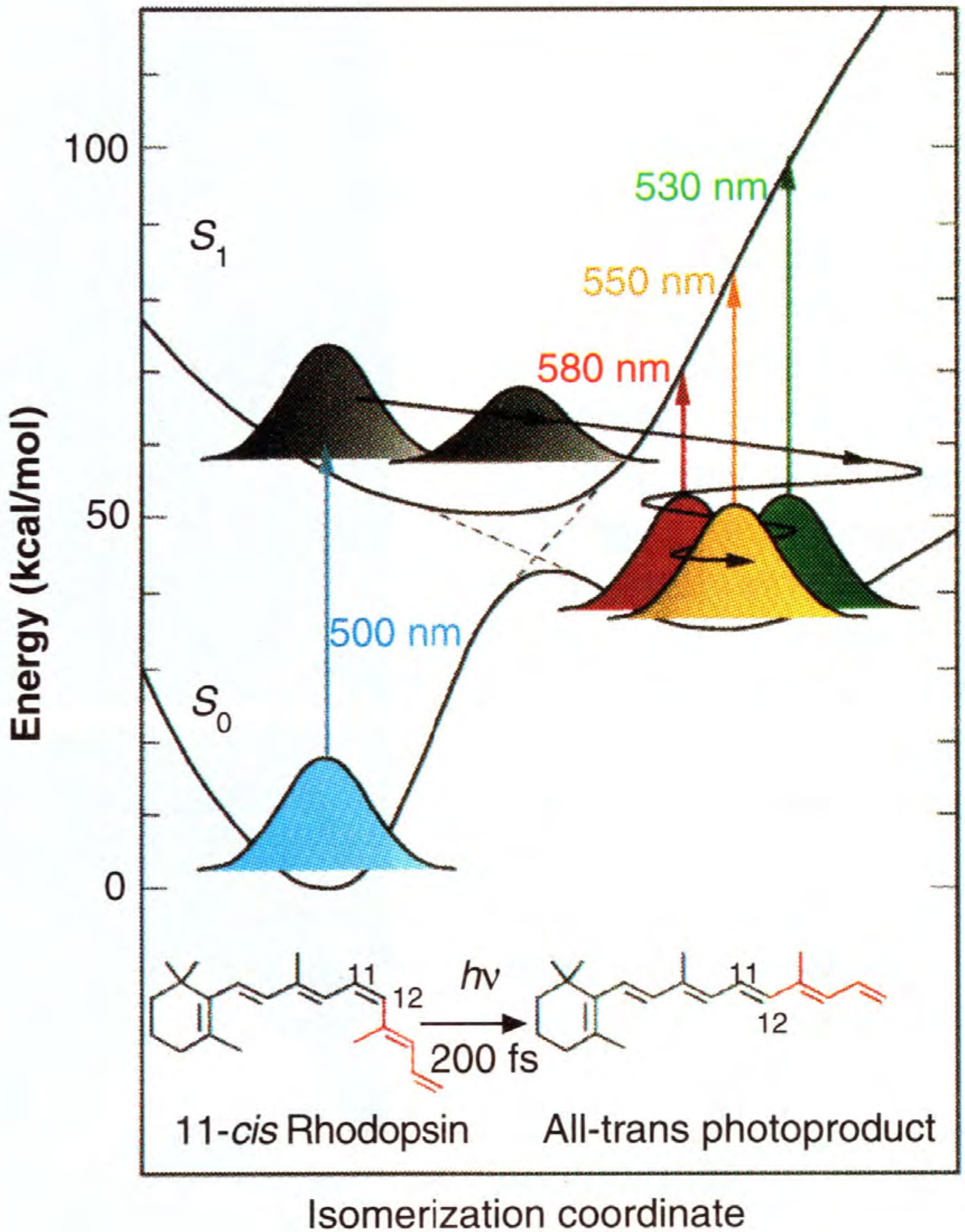
In visual pigment proteins, interaction of chromophore (11-*cis* retinal) with surrounding transmembrane helices is believed to modulate pigment absorption. Here, the helices are artifically thickened to emphasize cylindrical structure and cut away in front to reveal the chromophore inside ring

Harvesting Visible Photons: Vision and Rhodopsin



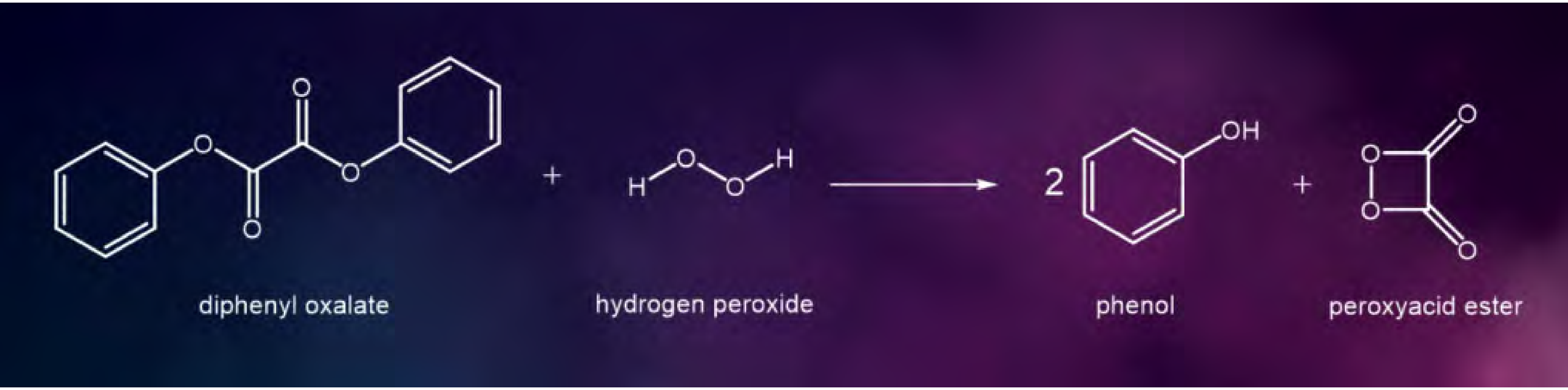


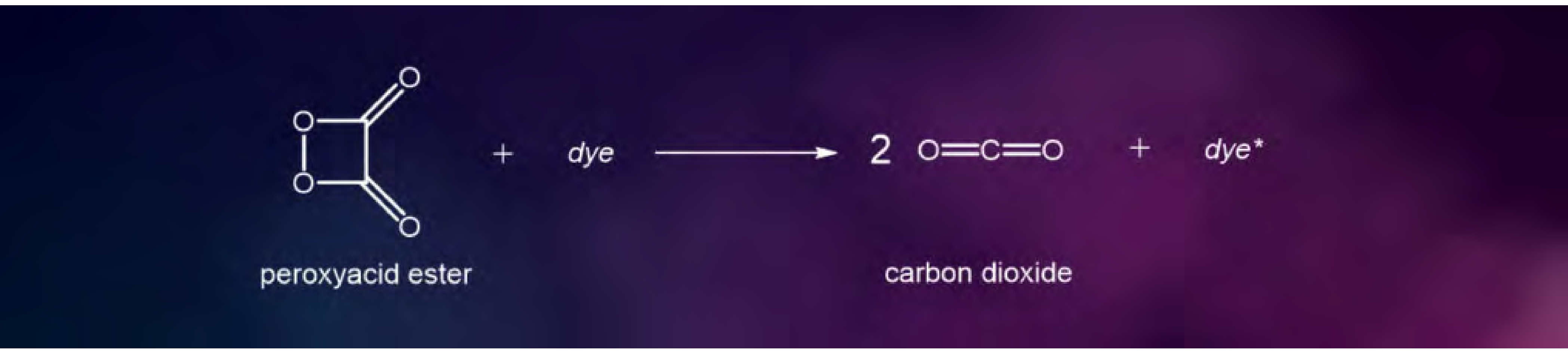
Harvesting Visible Photons: Vision and Rhodopsin



"Vibrationally Coherent Photochemistry in the Femtosecond Primary Event of Vision,"
C. V. Shank et al.
Science, pp 422-427, October 21, 1994

Glow Sticks



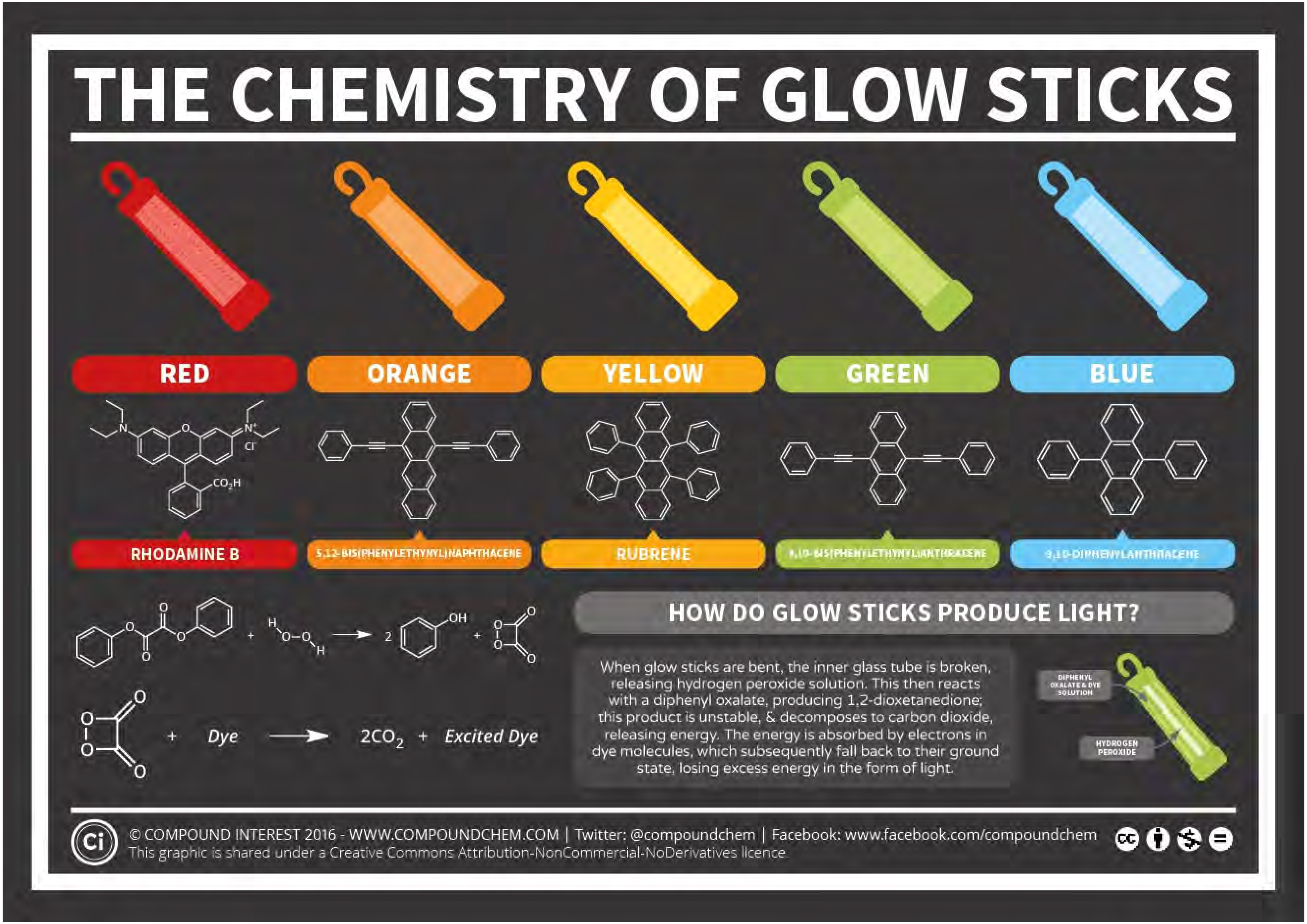


Discovered by Ed Chandross, Bell Labs, 1963

E. C. Chandross, "*A New Chemiluminescent System*" Tetrahedron Letters, **12**, pp 761-5 (1963).

"The patent attorney assigned to my department declined to file a patent, and I didn't realize how significant this really was."

Glow Sticks



THE CHEMISTRY OF GLOW STICKS
RED
ORANGE
YELLOW
GREEN
BLUE
RHODAMINE B
5,12-BIS(PHENYLETHYNYL)NAPHTHACENE
RUBRENE
9,10-BIS(PHENYLETHYNYL)ANTHRACENE
9,10-DIPHENYLANTHRACENE
+ Dye → 2CO2 + Excited Dye
HOW DO GLOW STICKS PRODUCE LIGHT?
When glow sticks are bent, the inner glass tube is broken, releasing hydrogen peroxide solution. This then reacts with a diphenyl oxalate, producing 1,2-dioxetanedione; this product is unstable, & decomposes to carbon dioxide, releasing energy. The energy is absorbed by electrons in dye molecules, which subsequently fall back to their ground state, losing excess energy in the form of light.
DIPHENYL OXALATE & DYE SOLUTION
HYDROGEN PEROXIDE
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