

Chem 115

Instrumental Analysis and Bioanalytical Chemistry

Lecture 5: Light-matter interactions

What's in this lecture?

- Finish solution chemistry
- Electromagnetic radiation
- Light-matter interactions

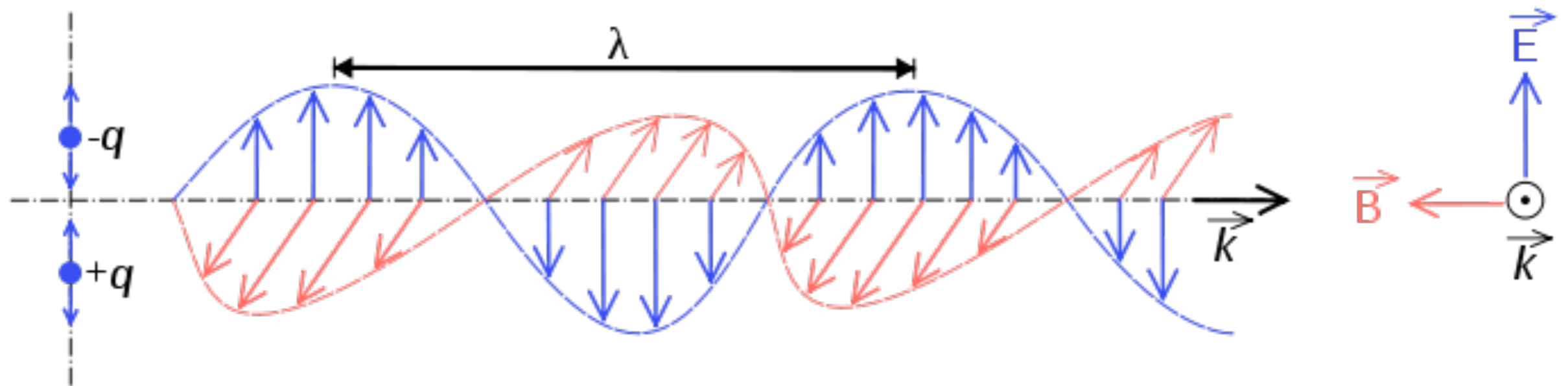
Activity coefficients at 25° C

Ion	$\alpha_x, \text{ nm}$	0.001	0.005	0.01	0.05	0.1
H ₃ O ⁺	0.9	0.967	0.933	0.914	0.86	0.83
Li ⁺ , C ₆ H ₅ COO ⁻	0.6	0.965	0.929	0.907	0.84	0.80
Na ⁺ , IO ₃ ⁻ , HSO ₃ ⁻ , H ₂ PO ₄ ⁻ , H ₂ AsO ₄ ⁻ , OAc ⁻	0.4	0.964	0.928	0.902	0.82	0.78
OH ⁻ , F ⁻ , SCN ⁻ , HS ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻	0.35	0.964	0.926	0.900	0.81	0.76
K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , HCOO ⁻	0.3	0.964	0.925	0.899	0.80	0.76
Rb ⁺ , Cs ⁺ , Tl ⁺ , Ag ⁺ , NH ₄ ⁺	0.25	0.964	0.924	0.898	0.80	0.75
Mg ²⁺ , Be ²⁺	0.8	0.872	0.755	0.69	0.52	0.45
Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺	0.6	0.870	0.749	0.675	0.48	0.40
Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻	0.5	0.868	0.744	0.67	0.46	0.38
Pb ²⁺ , CO ₃ ²⁻ , SO ₃ ²⁻ , C ₂ O ₄ ²⁻ ,	0.45	0.868	0.742	0.665	0.46	0.37
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻	0.40	0.867	0.740	0.660	0.44	0.36
Al ³⁺ , Fe ³⁺ , Cr ³⁺ , La ³⁺ , Ce ³⁺	0.9	0.738	0.54	0.44	0.24	0.18
PO ₄ ³⁻ , Fe(CN) ₆ ³⁻	0.4	0.725	0.50	0.40	0.16	0.095
Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺	1.1	0.588	0.35	0.255	0.10	0.065
Fe(CN) ₆ ⁴⁻	0.5	0.57	0.31	0.20	0.048	0.021

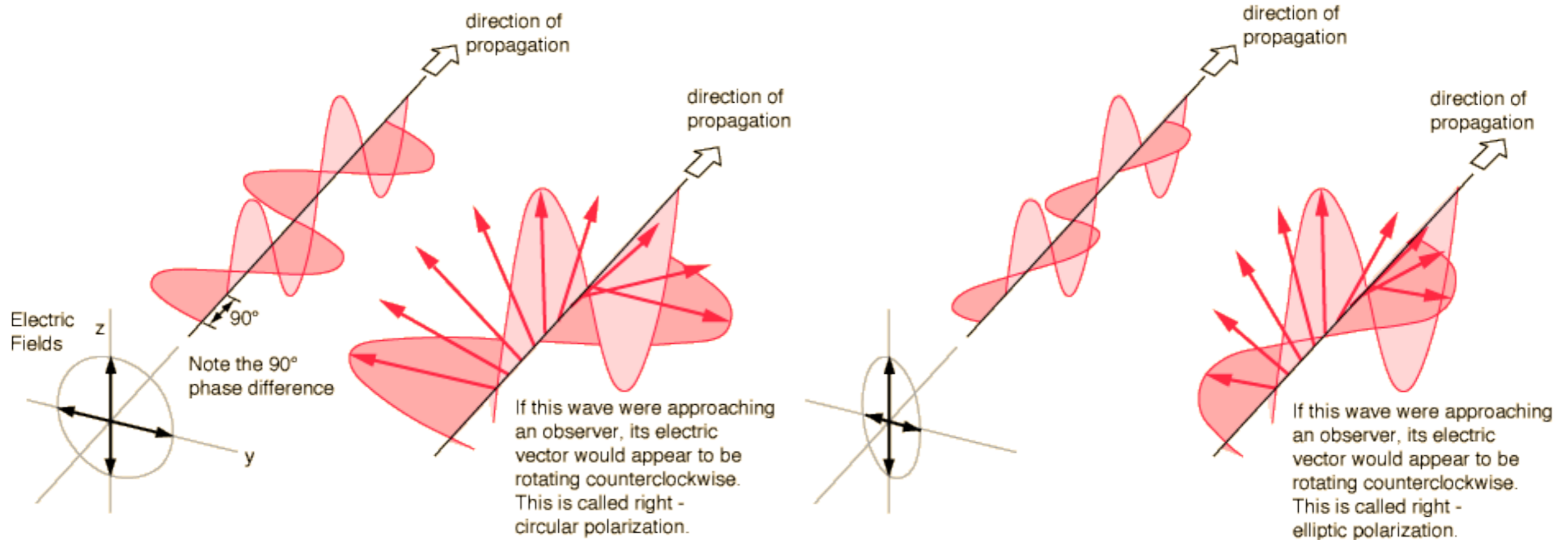
Activity example

What is the relative error introduced by neglecting activities in calculating the solubility of $\text{Ba}(\text{IO}_3)_2$ in a 0.033 M solution of $\text{Mg}(\text{IO}_3)_2$?

Electromagnetic radiation



Polarization



Circularly polarized

Elliptically polarized

See demo

Some important relations

$$c = \lambda \nu$$

$$E = h\nu$$

$$E = hc/\lambda$$

Where:

c = speed of light in vacuum = 3.00×10^8 m/s

h = Planck's constant = 6.626×10^{-34} J s

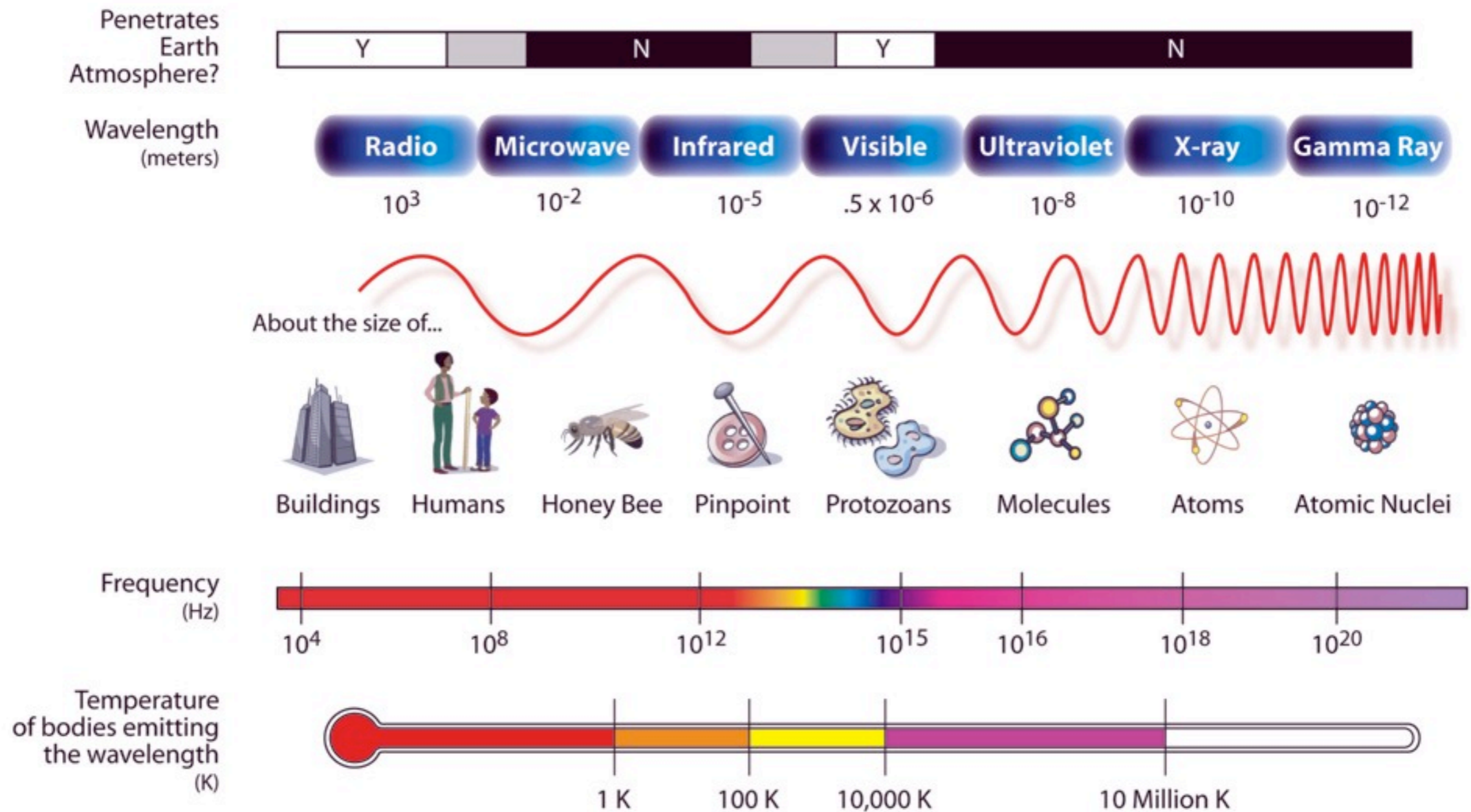
λ = wavelength of light

ν = frequency of light

E = energy of light

Common wavelength units

THE ELECTROMAGNETIC SPECTRUM



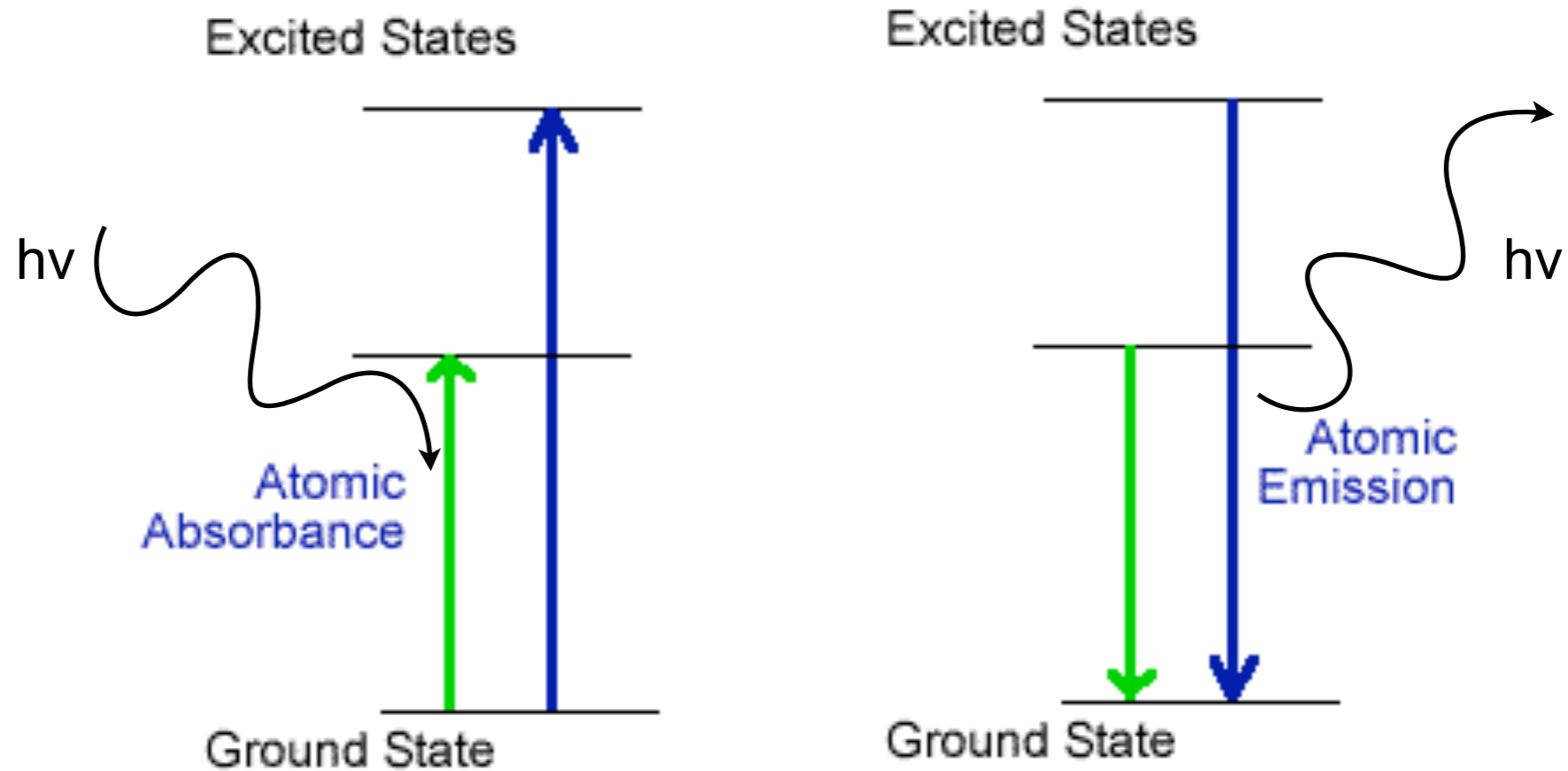
Light interacting with matter

Interaction	Radiation measured	Spectroscopic method
Absorption and transmission	Incident light, I_0 Transmitted light, I	Atomic absorption Molecular absorption
Absorption then emission	Emitted light, I'	Atomic fluorescence Molecular fluorescence Molecular phosphorescence
Scattering	Scattered light, I_s	Turbidity Nephelometry Raman
Reflection	Reflected light, I_R	Attenuated total reflection Diffuse reflection IR
Emission	Emitted light, I_e	Atomic emission Molecular emission Chemiluminescence

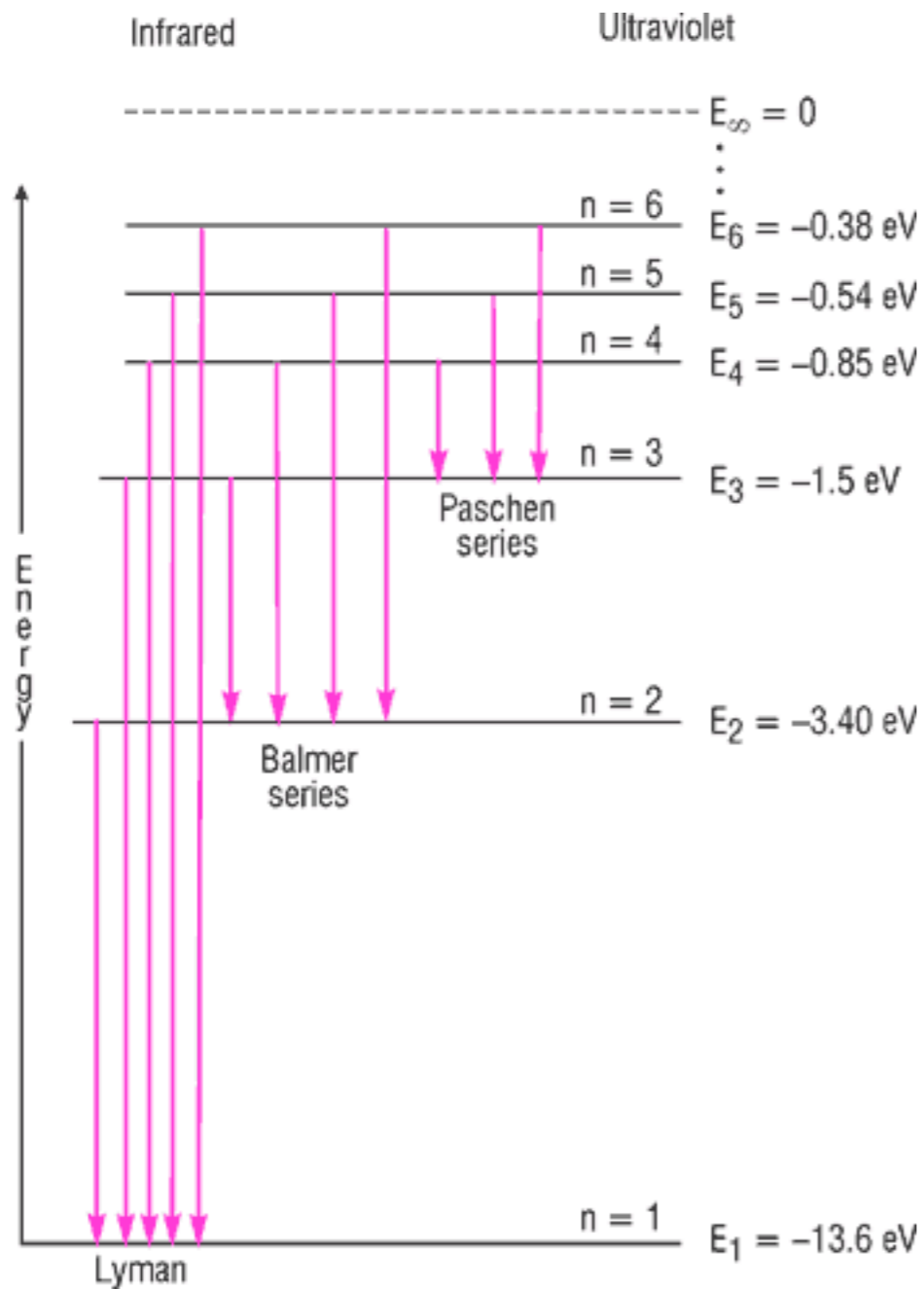
Types of transitions

Type of transition	Spectroscopic method	Wavelength range
Spin of nuclei in a magnetic field	NMR spectroscopy	0.5 - 10 meters
Rotation and vibration of molecules	Raman and IR spectroscopy	0.8 - 300 micrometers
Bonding/valence electron energy	UV/VIS spectroscopy	180 - 800 nanometers
Core electron energy	X-ray spectroscopy	0.1 - 100 angstroms

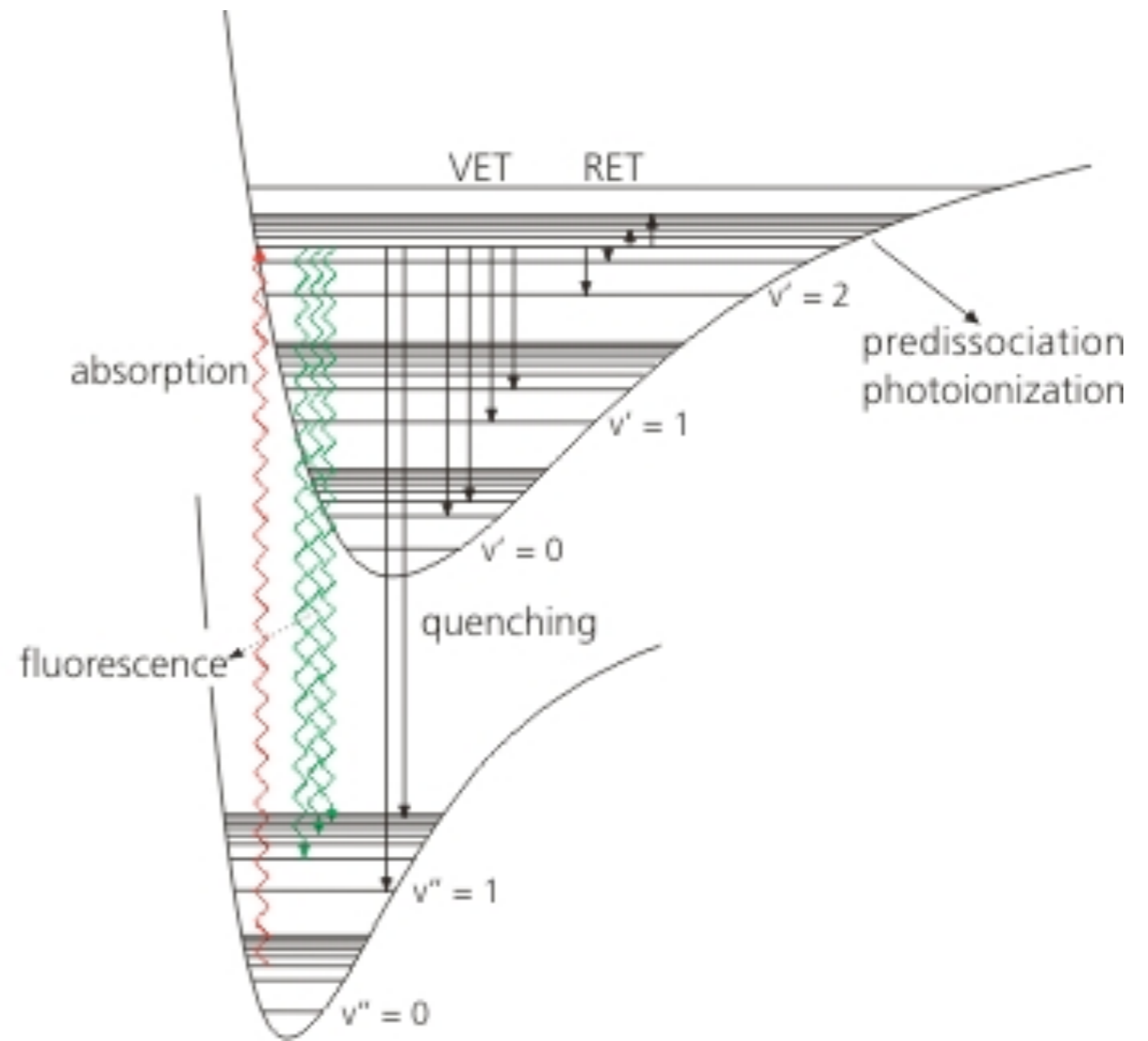
Excitation vs. emission



Energy diagrams



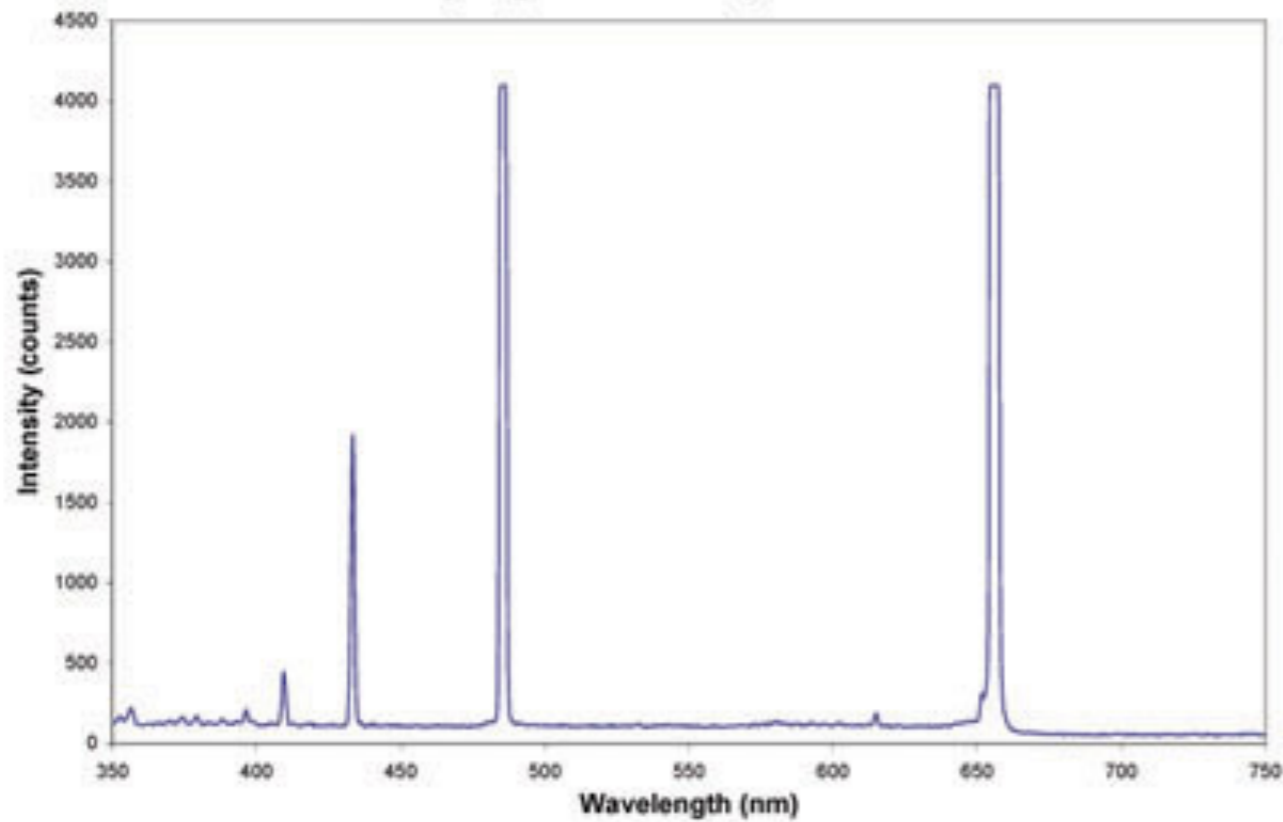
Atomic



Molecular

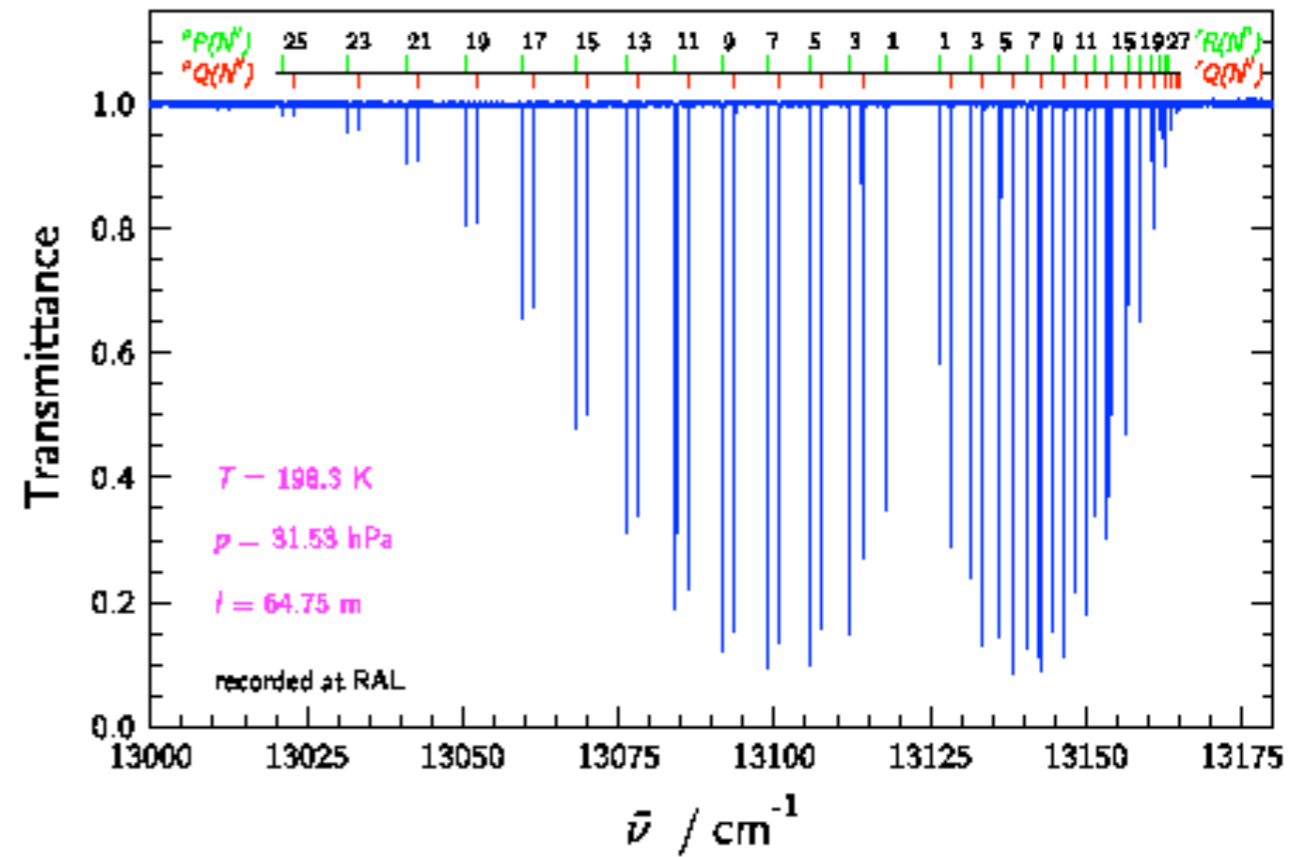
Spectra

Hydrogen Emission Spectrum



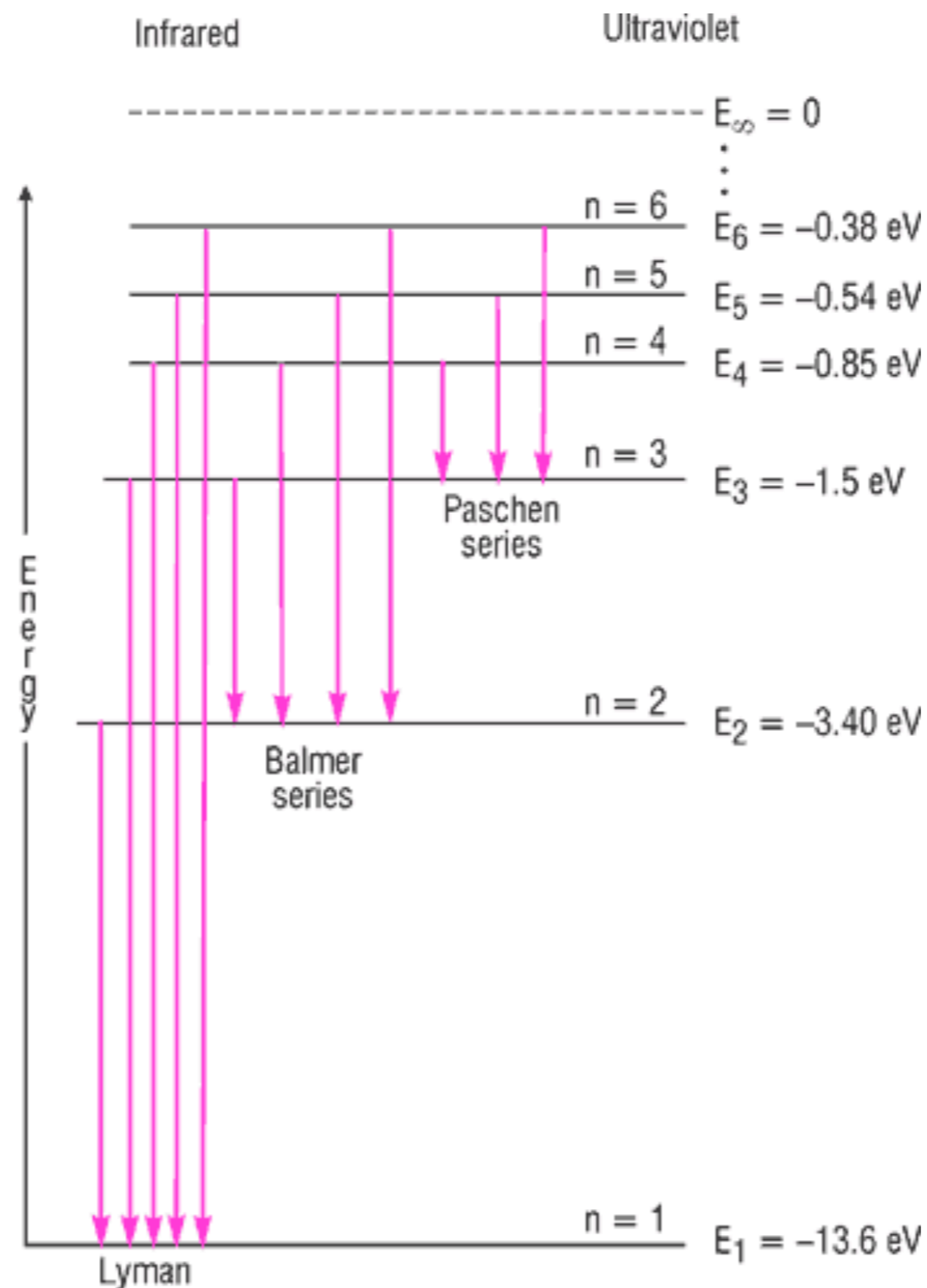
Atomic

O₂ A Band Spectrum, ${}^3\Sigma_g^-(v=0) \leftarrow {}^1\Sigma_g^+(v=0)$



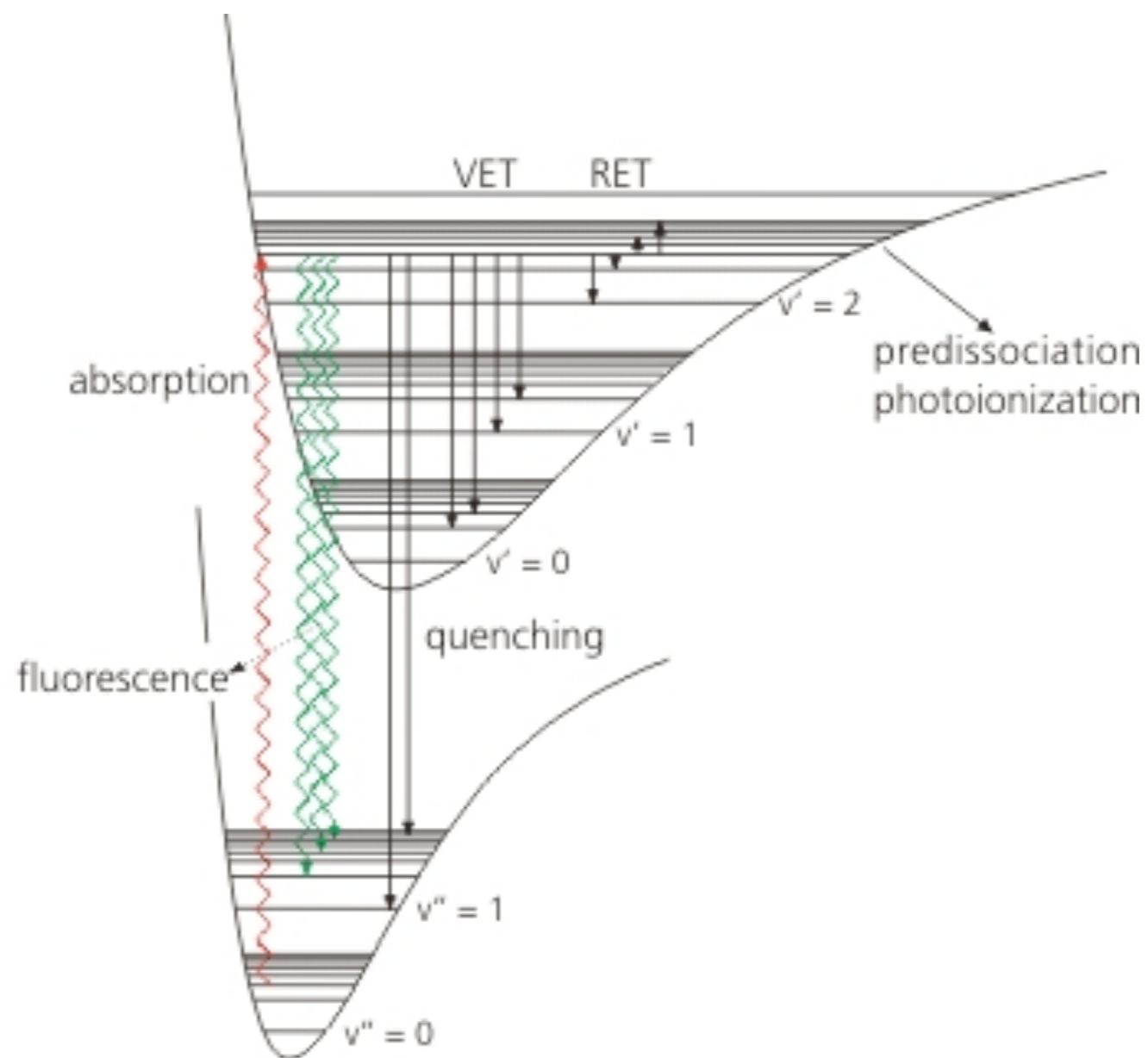
Molecular

Atomic spectroscopy

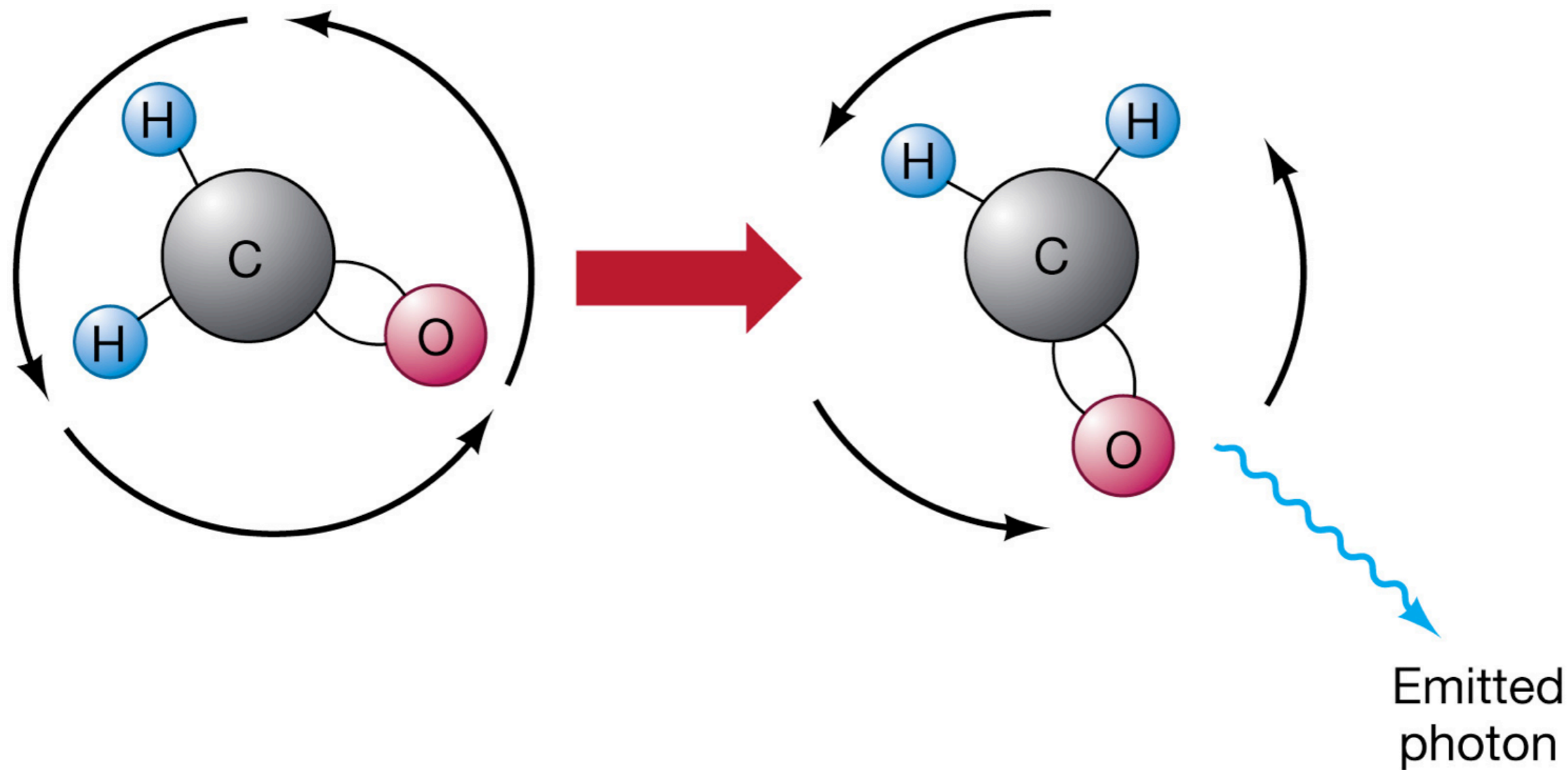


Hydrogen energy diagram

Molecular spectroscopy

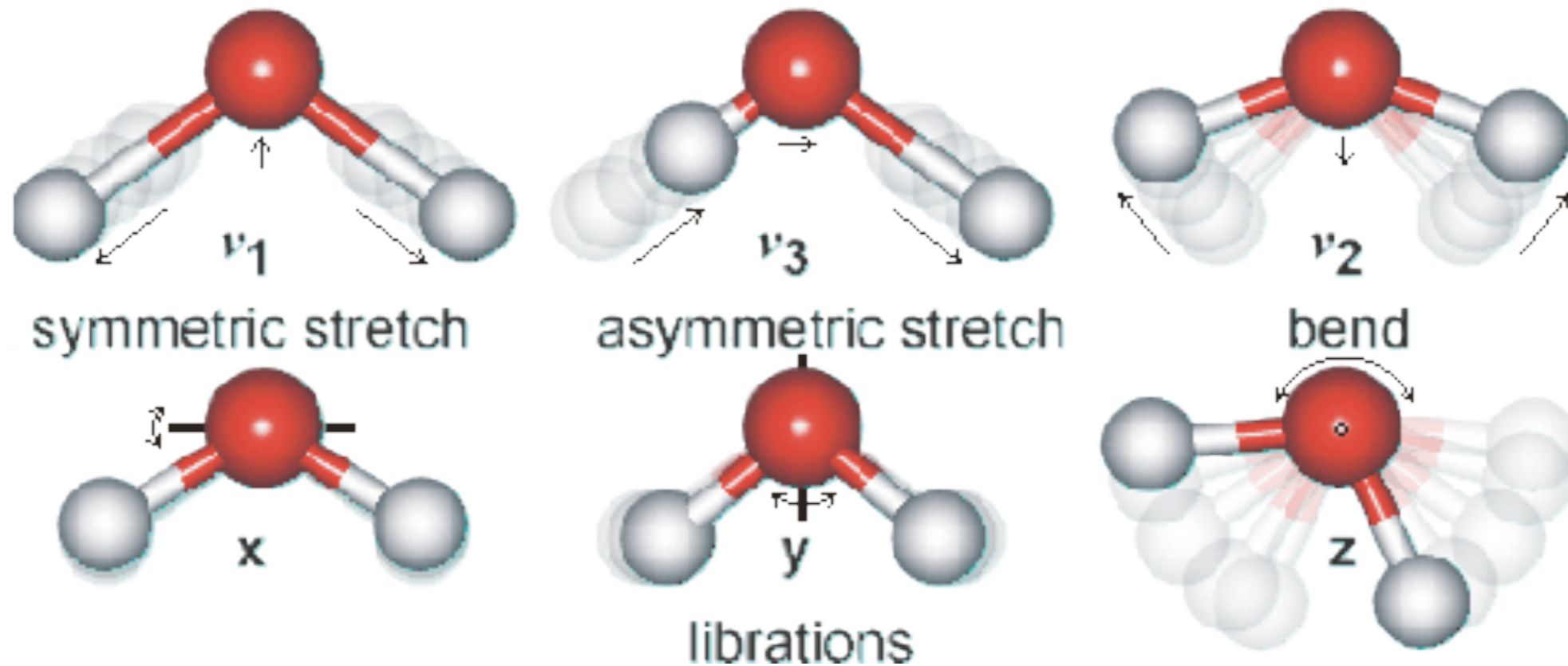


Rotational transitions

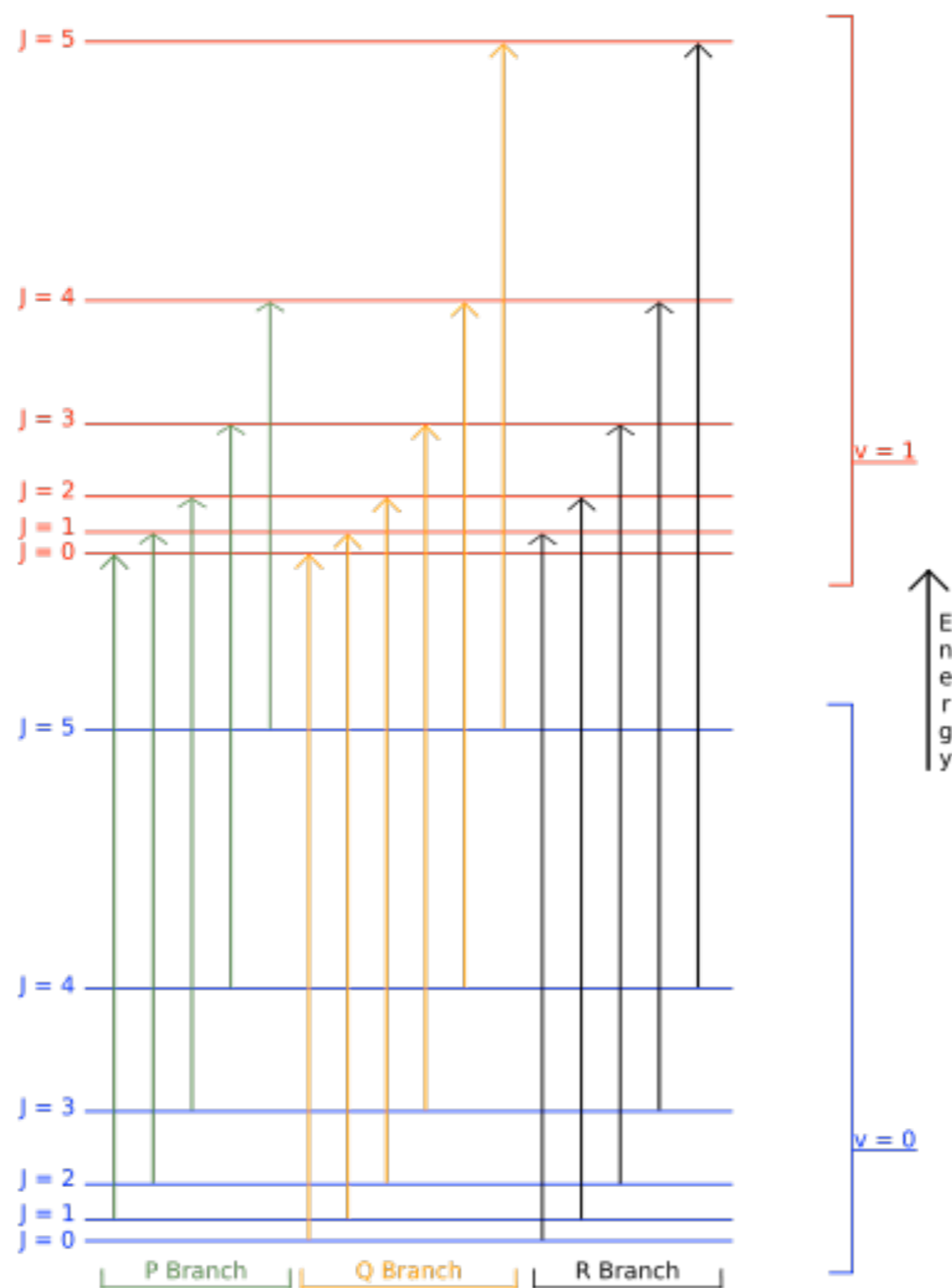


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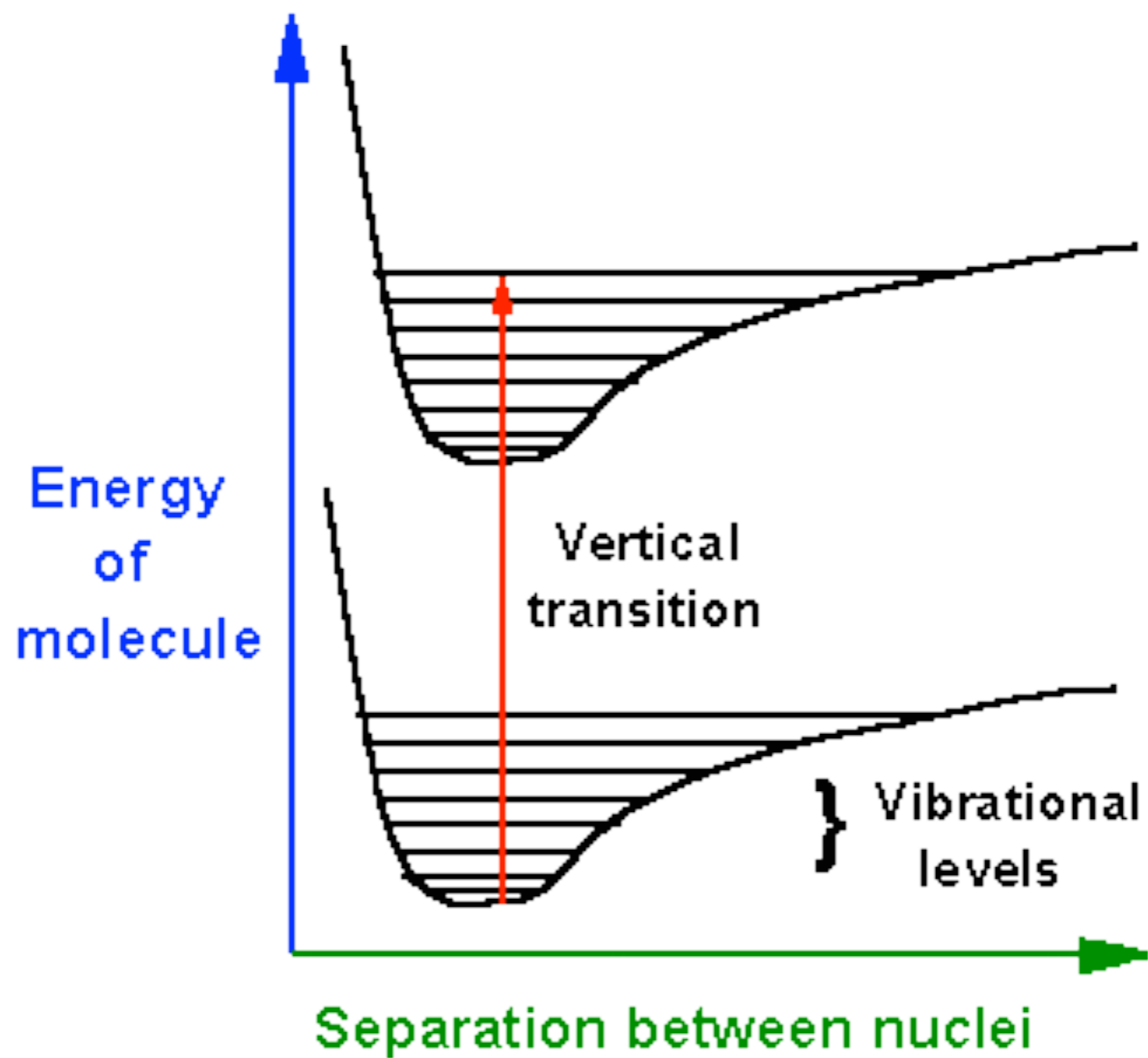
Vibrational transitions



Rovibrational spectroscopy



Electronic transitions



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