Structural determination – 1(B)

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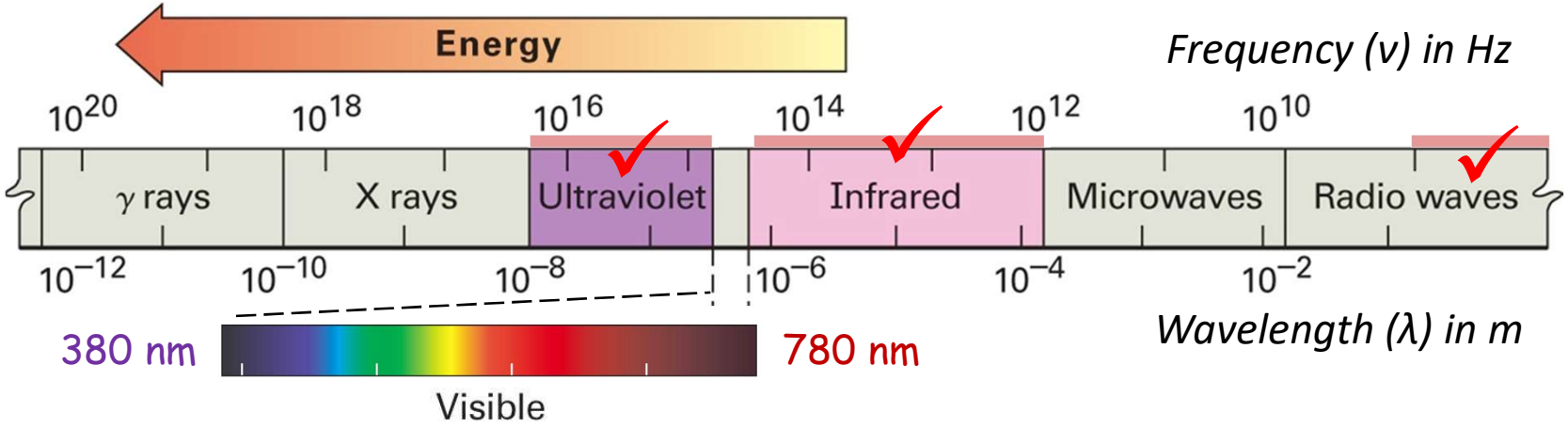
What properties are examined in IR?

Spectroscopic analyses of organic compounds

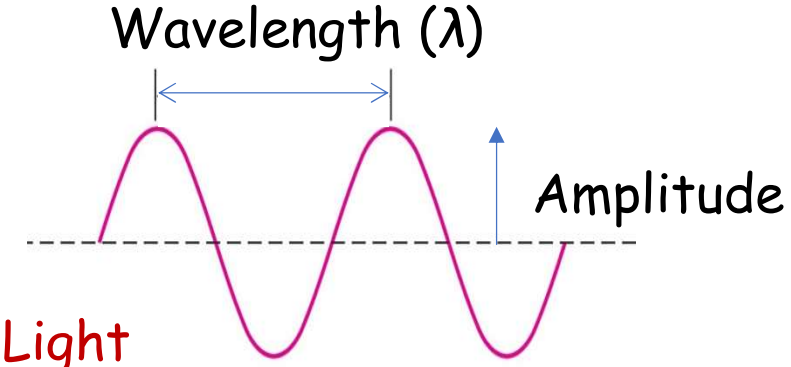
Technique	Electromagnetic radiation	Structure
Infrared spectrometry	Infrared light	Covalent bonds
Ultraviolet spectroscopy	Ultraviolet light	σ–σ^*, n–σ^*, π–π^*, n–π^* transitions
Nuclear magnetic resonance spectroscopy	Radio wave	Atomic nuclei in magnetic field



Properties of electromagnetic radiation – Wave-particle duality

Electromagnetic radiation has dual properties.

- ✓ Wave properties - In homogeneous media, electromagnetic radiation is a transverse wave, meaning that its oscillations are perpendicular to the direction of energy transfer and travel



Light speed

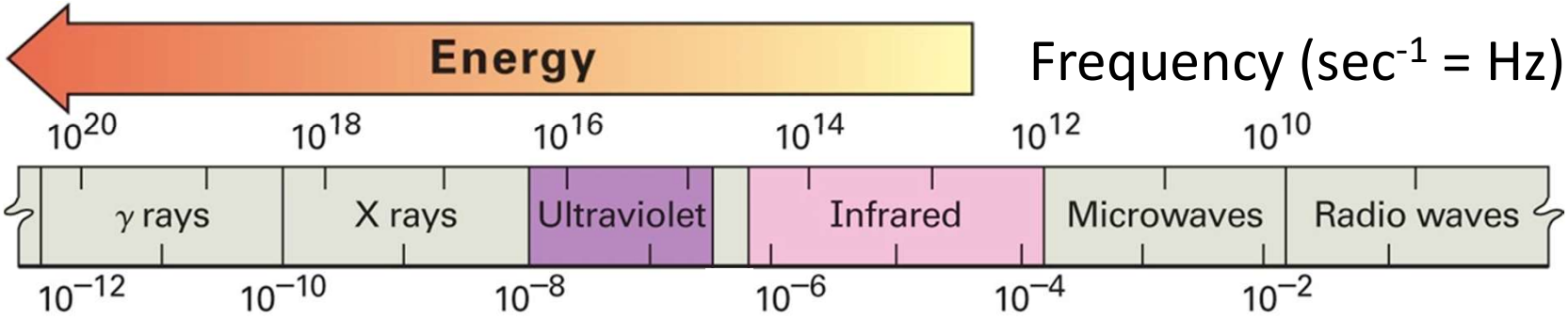
$C = \lambda \cdot \nu = 2.998 \times 10^8$ m/sec

Frequency (sec^{-1} = Hz)

- ✓ Particle properties - The particle of light has the name photon, like other particles such as the electron and proton. Thus, a photon is a single quantum of light

Quantum (plural: quanta)

The minimum amount of any physical property involved in an interaction. This means that the magnitude of the physical property can take on only discrete values consisting of integer multiples of one quantum.



A photon, or any other form of electromagnetic radiation, has the quantum of energy (ε) that is in direct proportional to its frequency (ν)

$$\varepsilon = h \cdot \nu$$

Planck constant

$6.62607015 \times 10^{-34}$ J·s

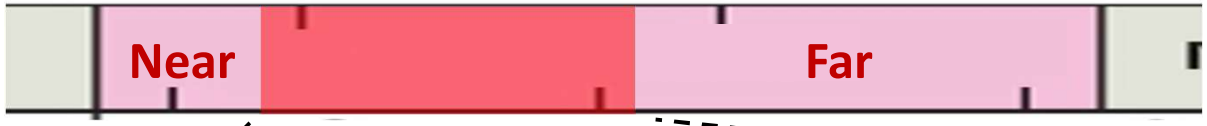
$E = N_A \times \varepsilon = 4 \times 10^{-10} \cdot \nu$ (J·s/mol)

Infrared spectroscopy

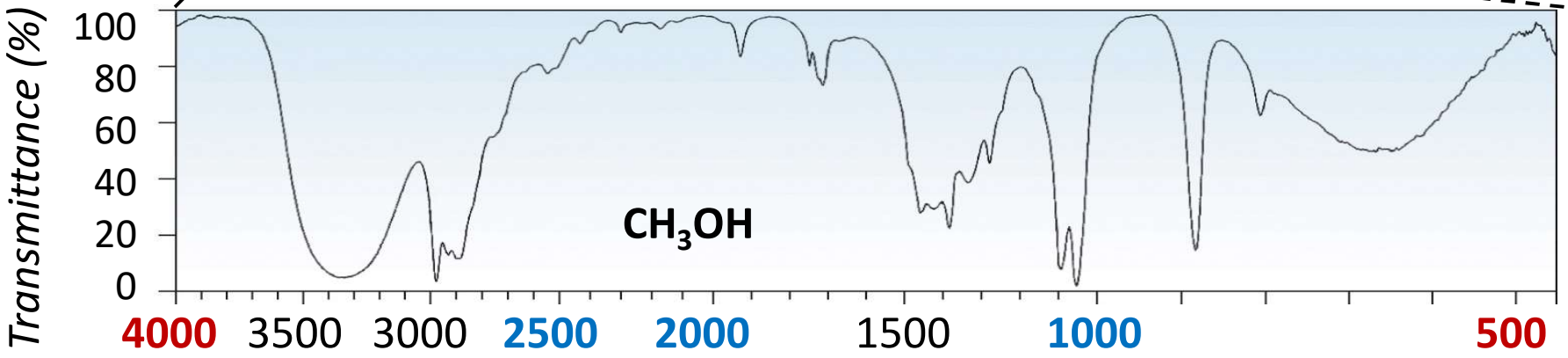
$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{C} \approx \frac{\nu\,(^{1}/_{sec})}{3\times10^{8}(^{m}/_{sec})\cdot 100(^{cm}/_{m})} \approx 33\cdot\frac{\nu}{10^{12}}\,(cm^{-1})$$

(3333) 10^{14} (333) 10^{13} (33) 10^{12}

(ν; sec^{-1} = Hz)
Frequency
∝ Energy



10^{-6} 10^{-5} 10^{-4} Wavelength (λ; m)



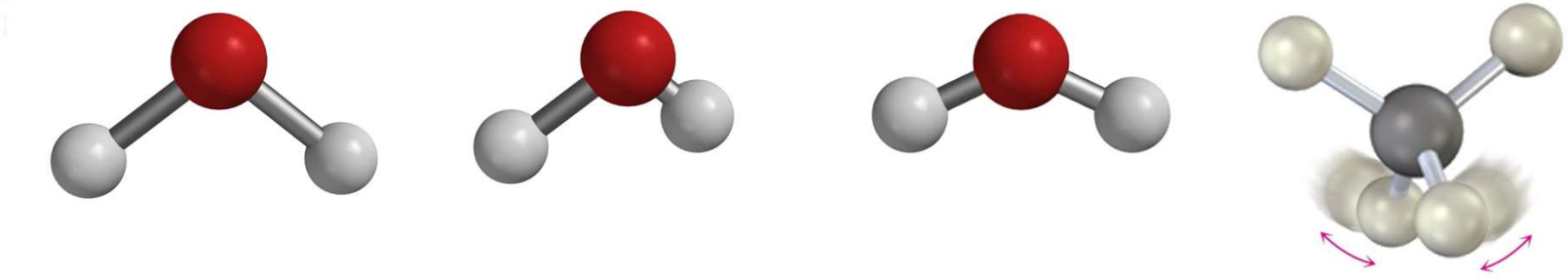
Wavenumber ($\tilde{\nu}$; cm^{-1}) ∝ Frequency

100% at top

What structures absorb the energy in IR?

The absorption of infrared quanta causes vibration of covalent bonds

Upon absorption of the infrared radiation of a specific frequency, molecules stretch or bend if the frequency of the radiation matches the frequency of the vibration

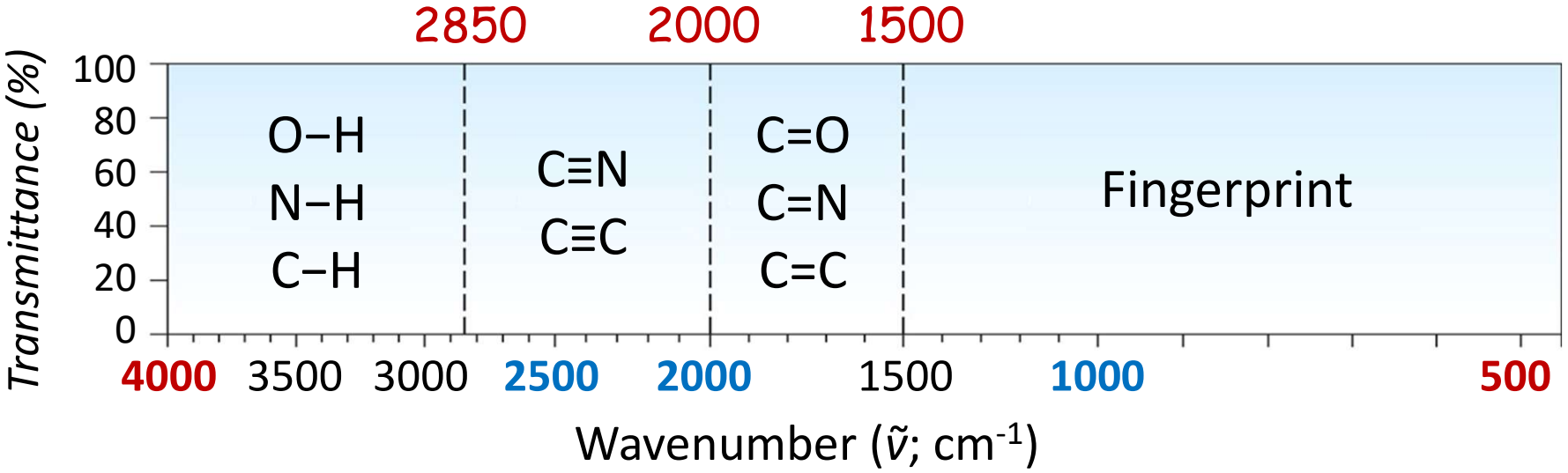


Symmetric stretching | Antisymmetric stretching | In-plane bending | Out-of-plane bending

How do we interpret the IR spectra?

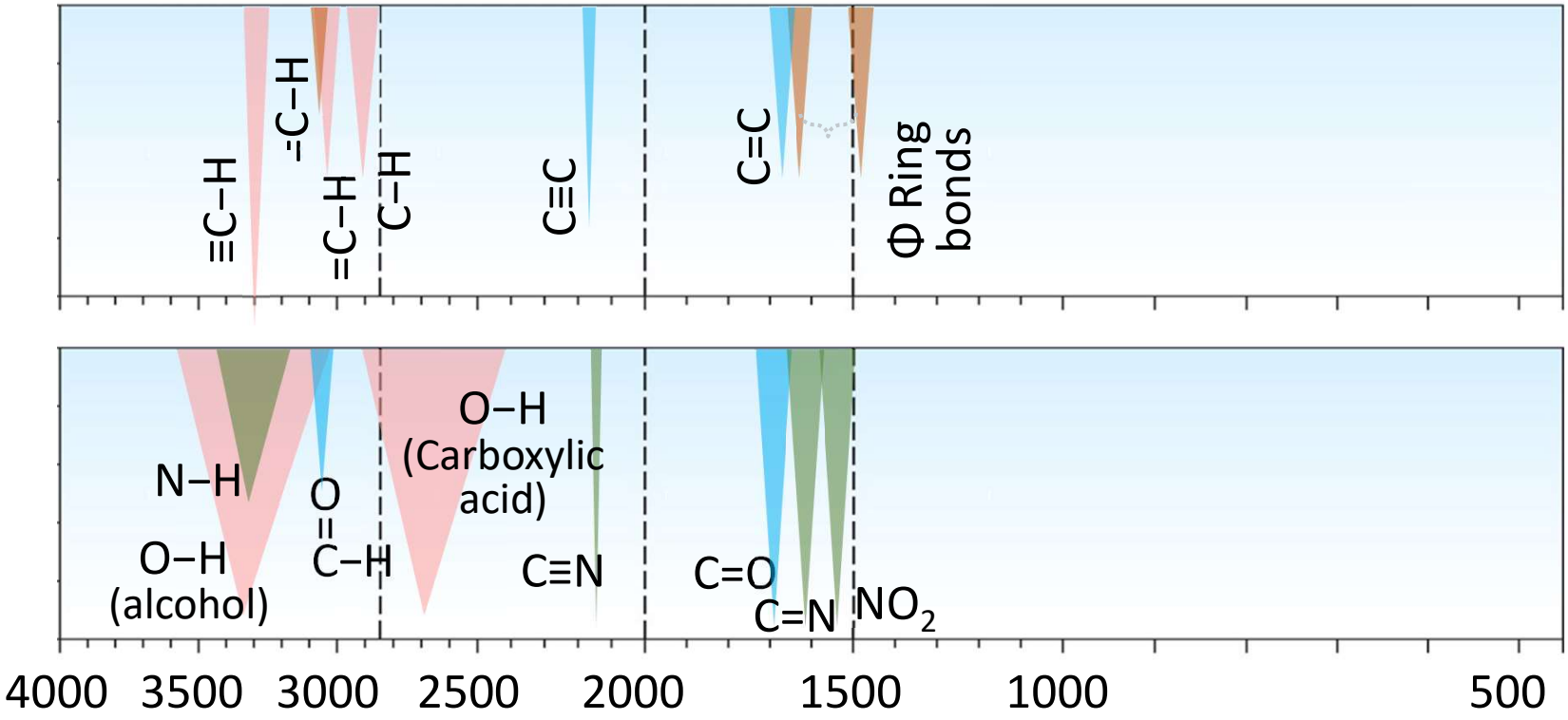
Interpret infrared spectra

Most functional groups have characteristic *IR* absorption bands that do not change from one compound to another



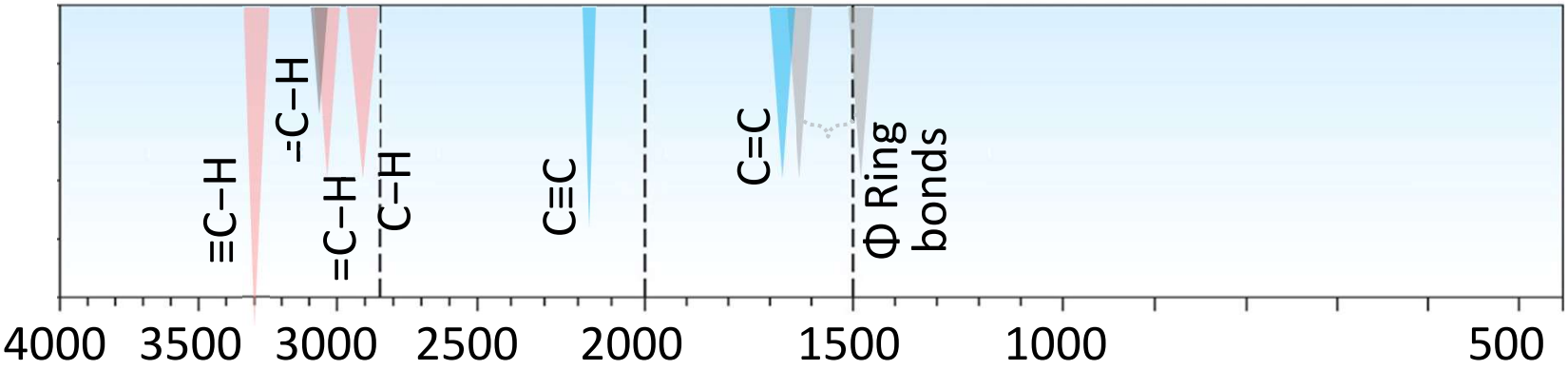
NP2, NP3

Infrared absorption frequencies in organic chemistry



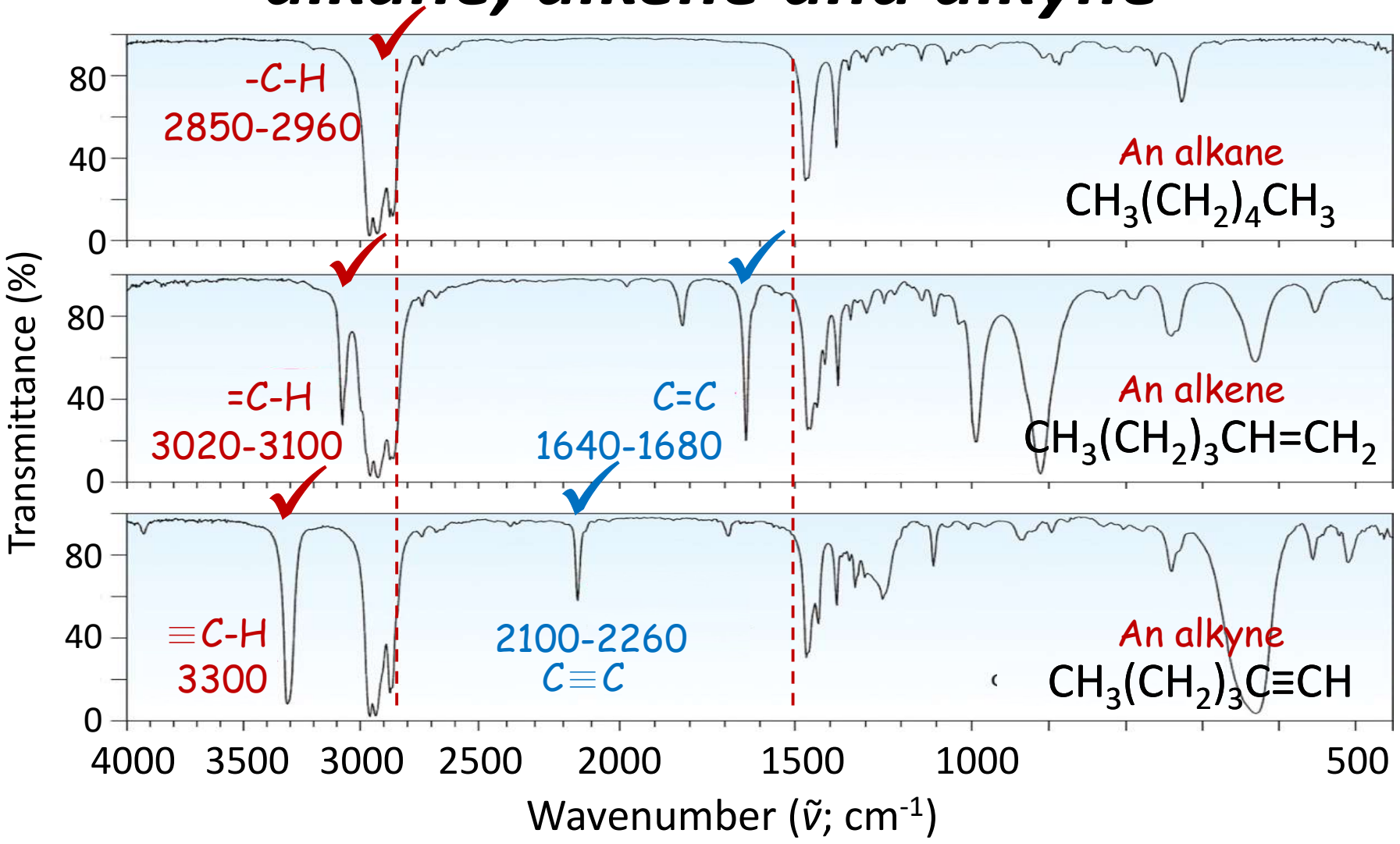
NP2

Infrared absorption frequencies of hydrocarbons



Group	Class	Frequency, cm^{-1}	Signal	Group	Class	Frequency (cm^{-1})	Signal
C-H	Alkane	2850-2960	M	≡C-H	Alkyne	3300	S
=C-H	Alkene	3020-3100	M	C≡C	Alkyne	2100-2260	M
C=C	Alkene	1640-1680	M	=C-H	Arene	3030	W
W: weak, M: medium, S: strong				Φ Ring bonds	Arene	1450-1600	M

IR characteristics in alkane, alkene and alkyne



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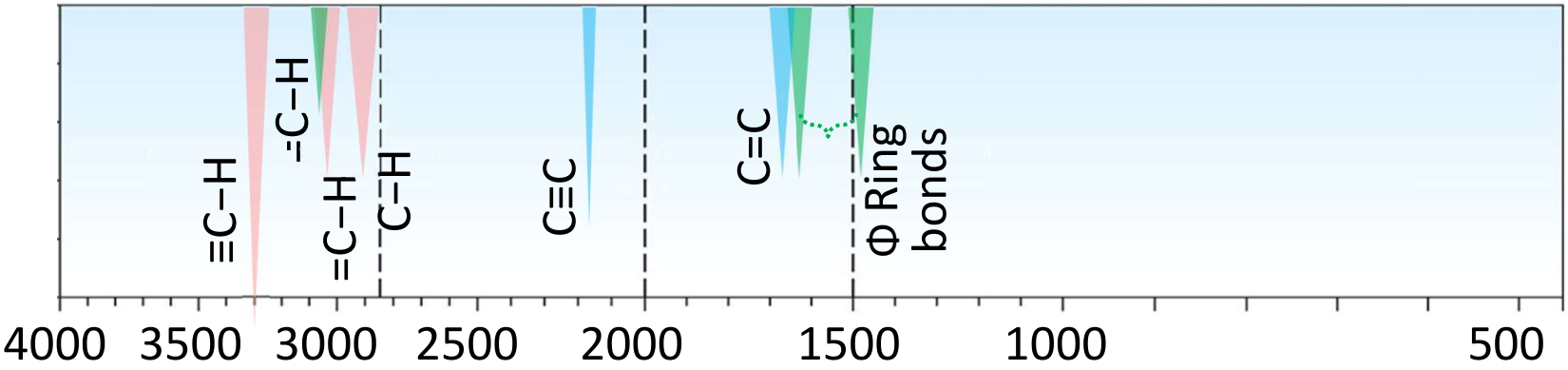

Bond	Class	Frequency, cm^{-1}	Signal	Bond	Class	Frequency (cm^{-1})	Signal
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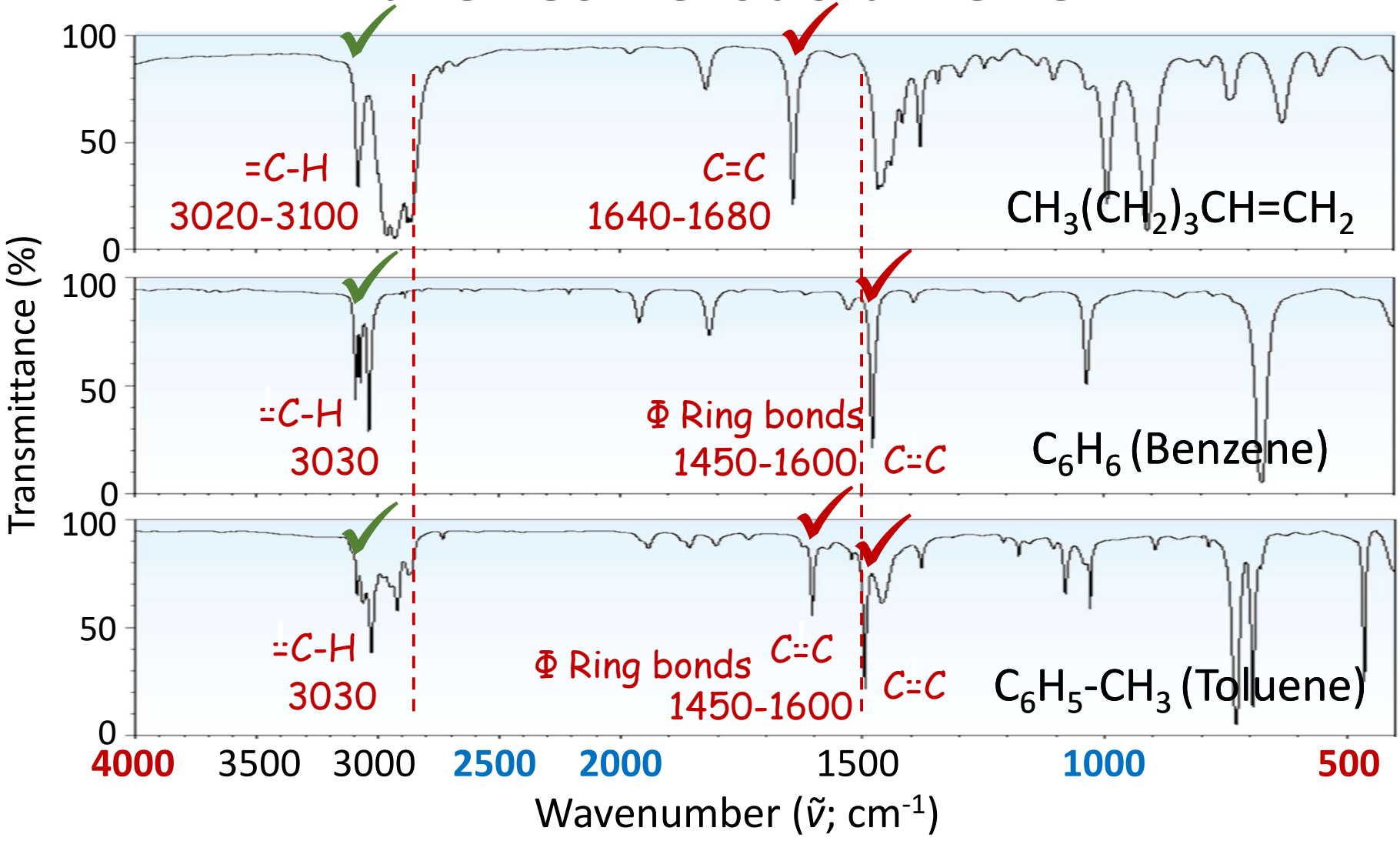
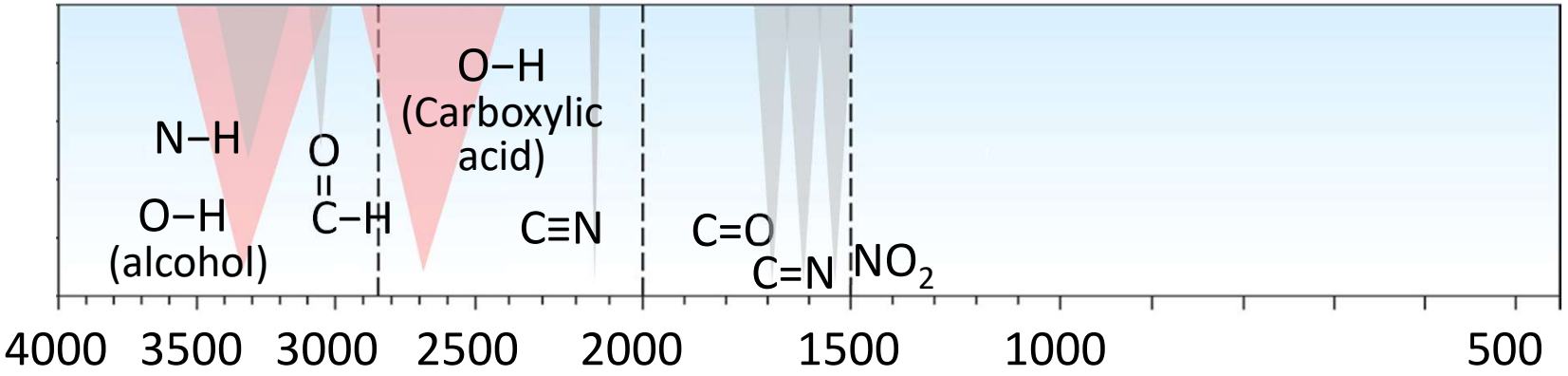
=C-H	Alkene	3020-3100	M	C≡C 3	Alkyne	2100-2260	M
C=C 2	Alkene	1640-1680	M ✓	=C-H	Arene	3030	W
W: weak, M: medium, S: strong ✓				Φ Ring bonds 1 1/2	Arene	1450-1600	M

IR characteristics in arenes versus alkene



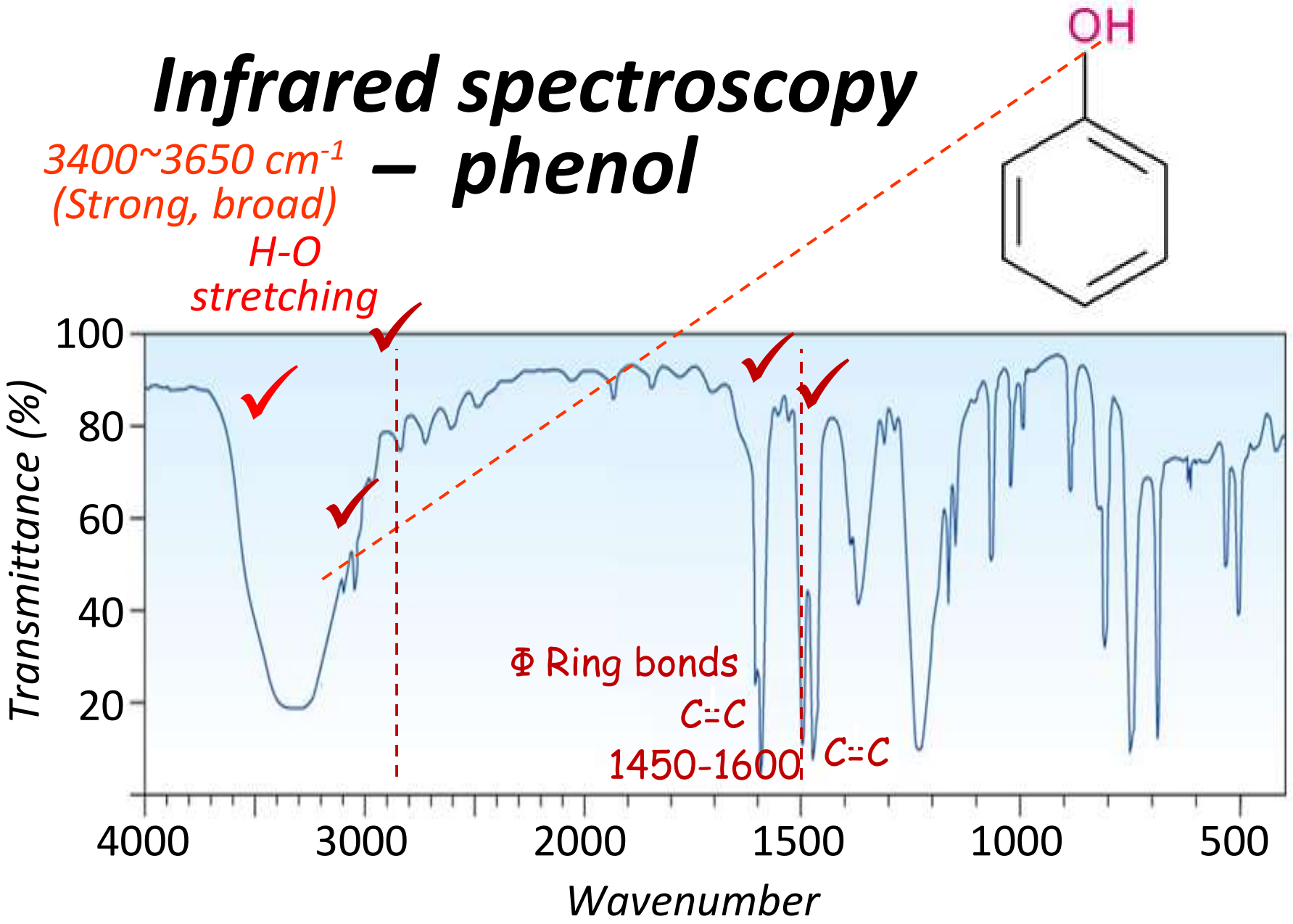
NP3

Infrared absorption frequencies of oxygen-containing substances



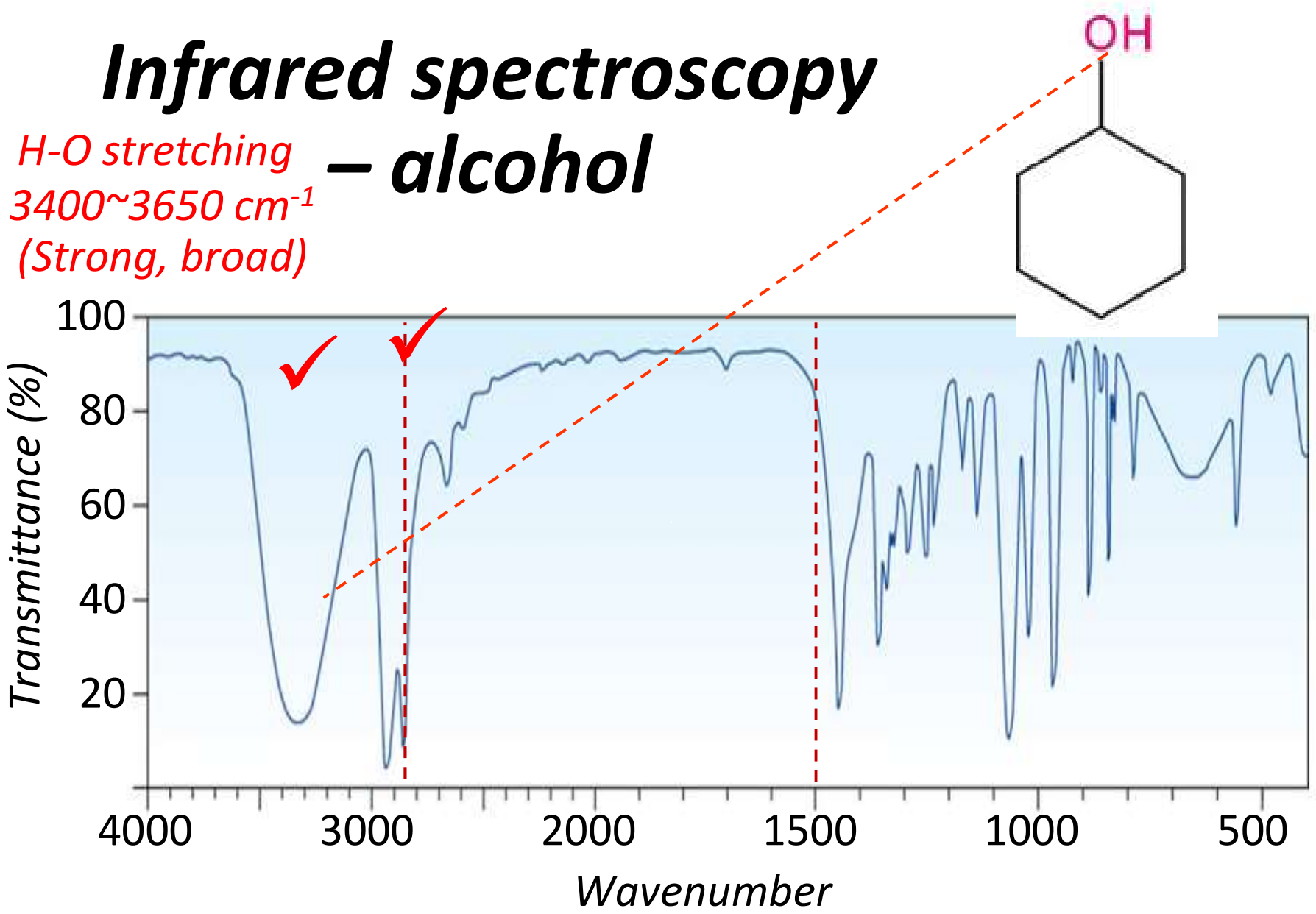
Bond	Functional class	Frequency cm^{-1}	Signal	Bond	Class	Frequency cm^{-1}	Signal
O-H	Alcohol	3400-3650	S&B	N-H	Amine	3300-3500	M
O-H	Carboxylic acid	2500-3100	S&B	C=N	Imine	1610-1690	S
=C-H	Aldehyde	3020-3100	M	C≡N	Nitrile	2210-2260	M
C=O	Aldehyde, ketone, ester, amide and carboxylic acid	1670-1780	S	NO_2	Nitro	1540	S
				W: weak, M: medium, S: strong			

Infrared spectroscopy – phenol



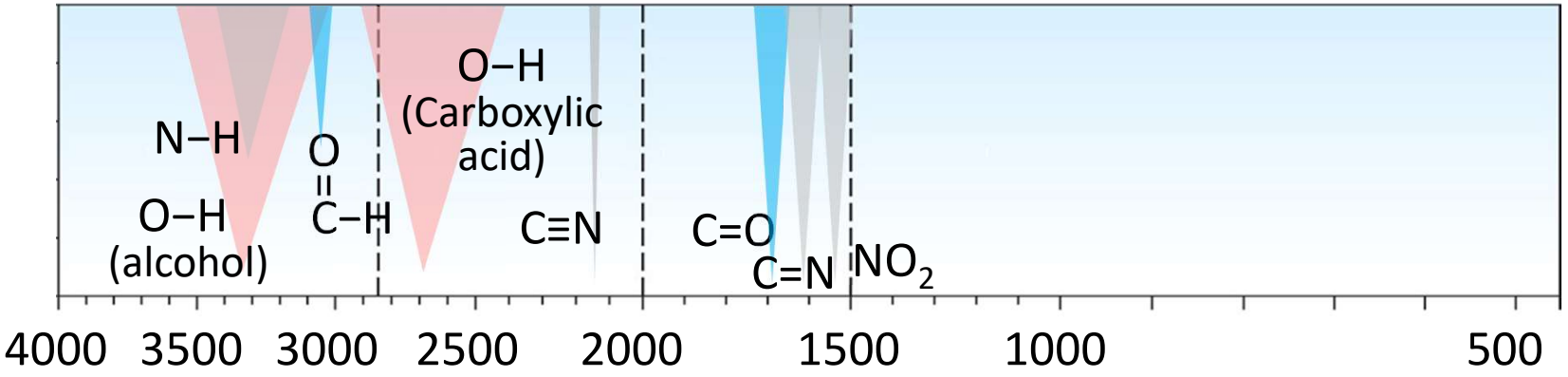
Infrared spectroscopy – alcohol

H-O stretching
3400~3650 cm^{-1}
(Strong, broad)



NP3

Infrared absorption frequencies of oxygen-containing substances



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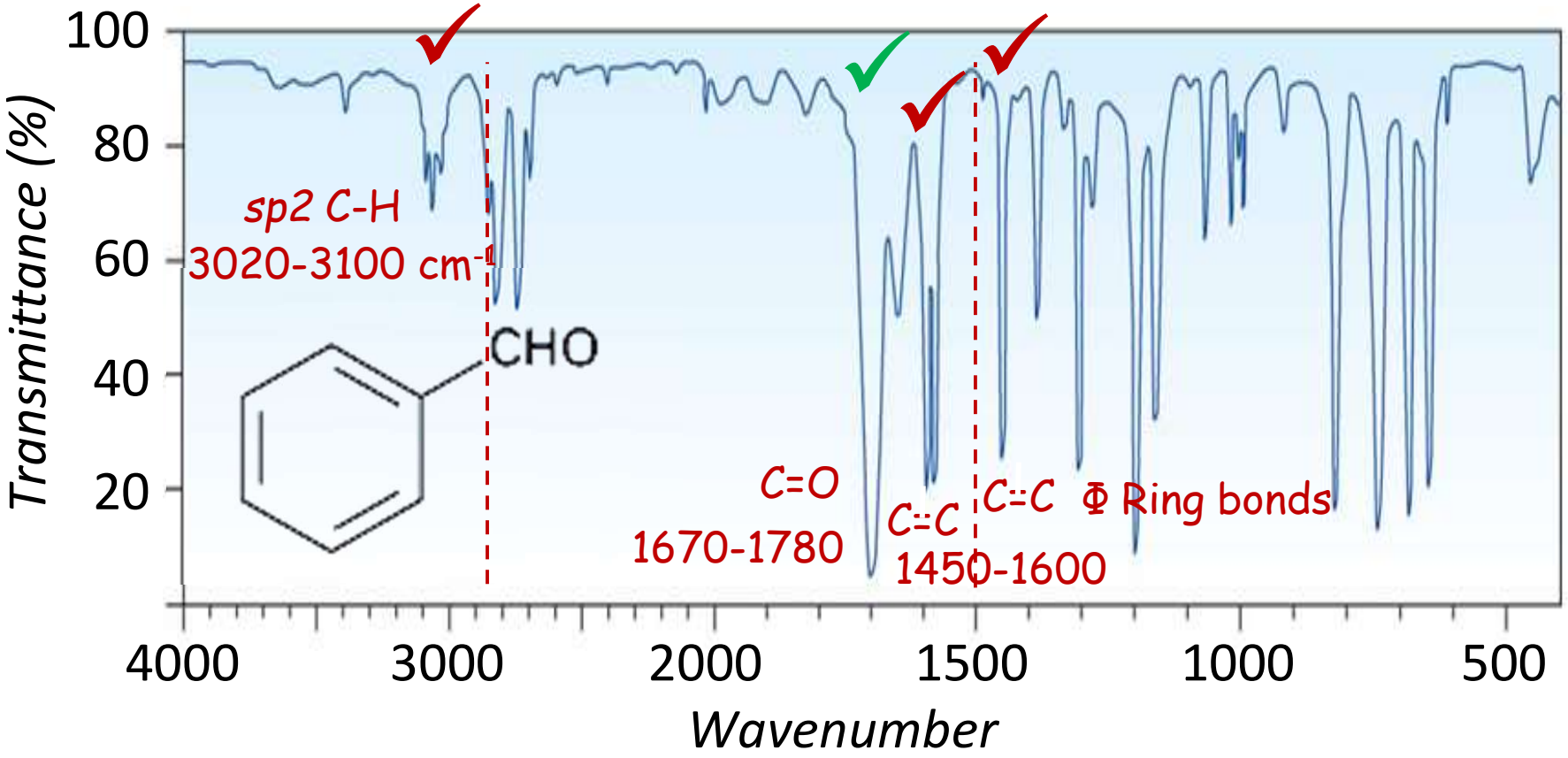
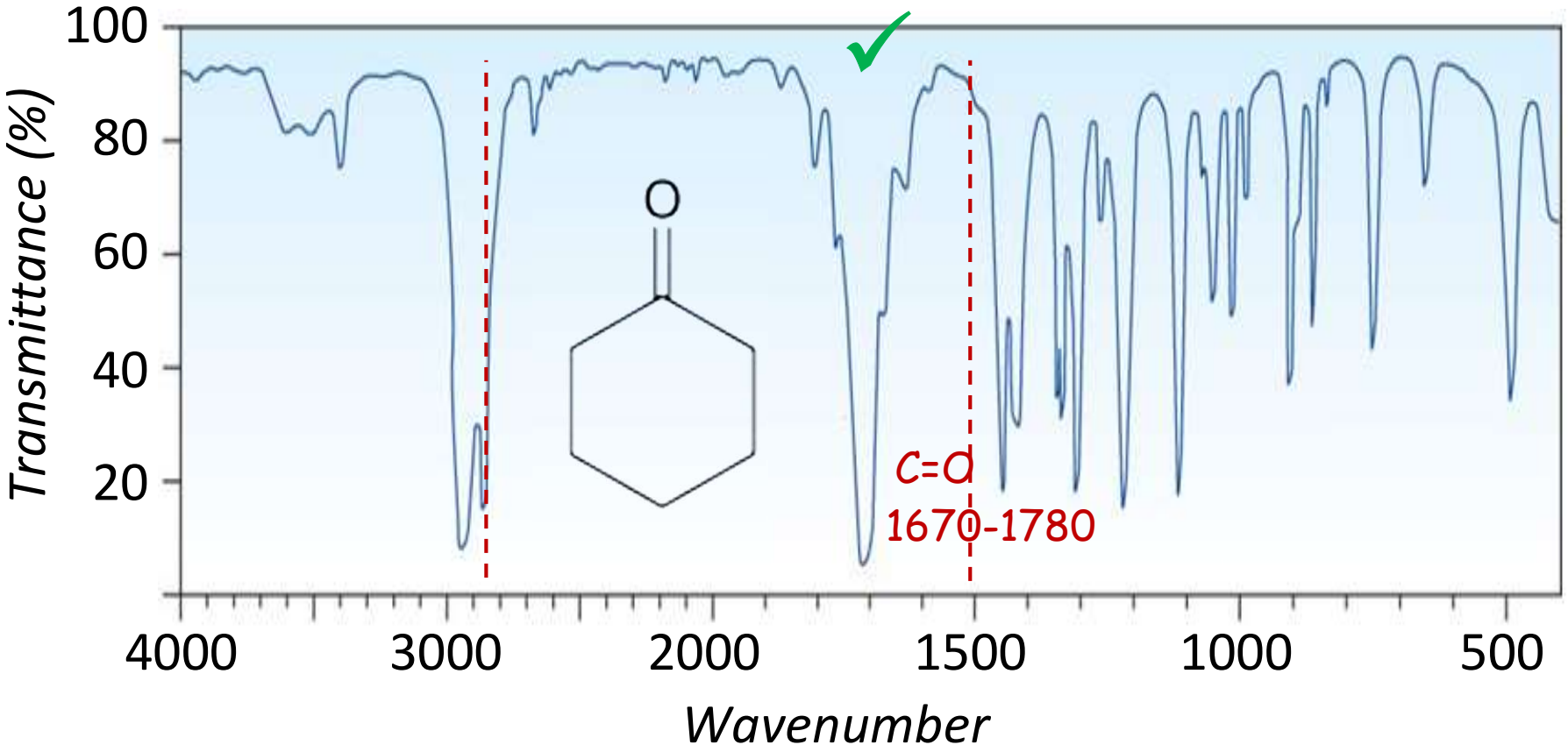
✓ C=O	Aldehyde, ketone, ester, amide and carboxylic acid	1670-1780	S	NO_2	Nitro	1540	S
				W: weak, M: medium, S: strong			

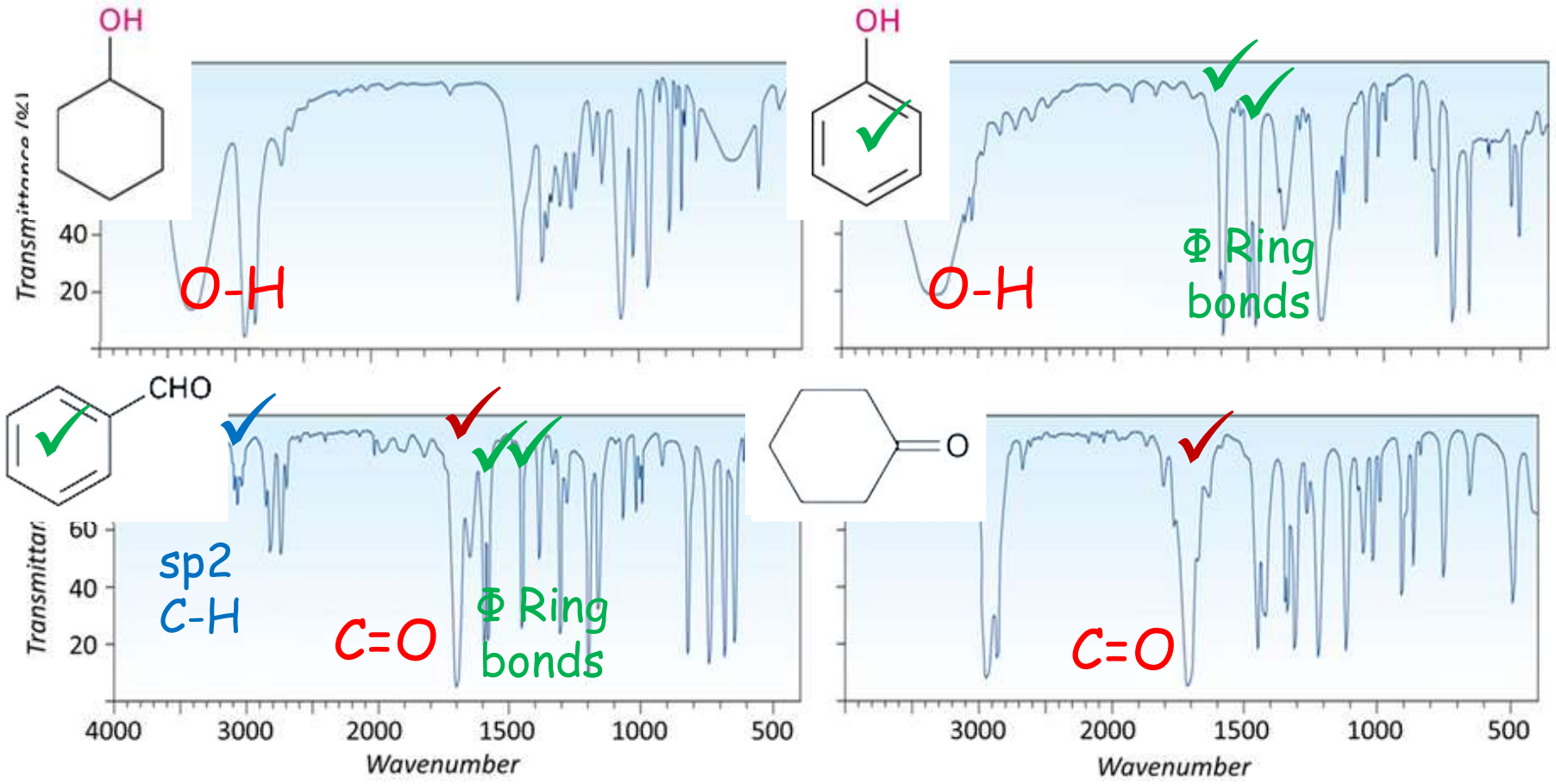
Infrared spectroscopy - aldehyde



Infrared spectroscopy - ketone

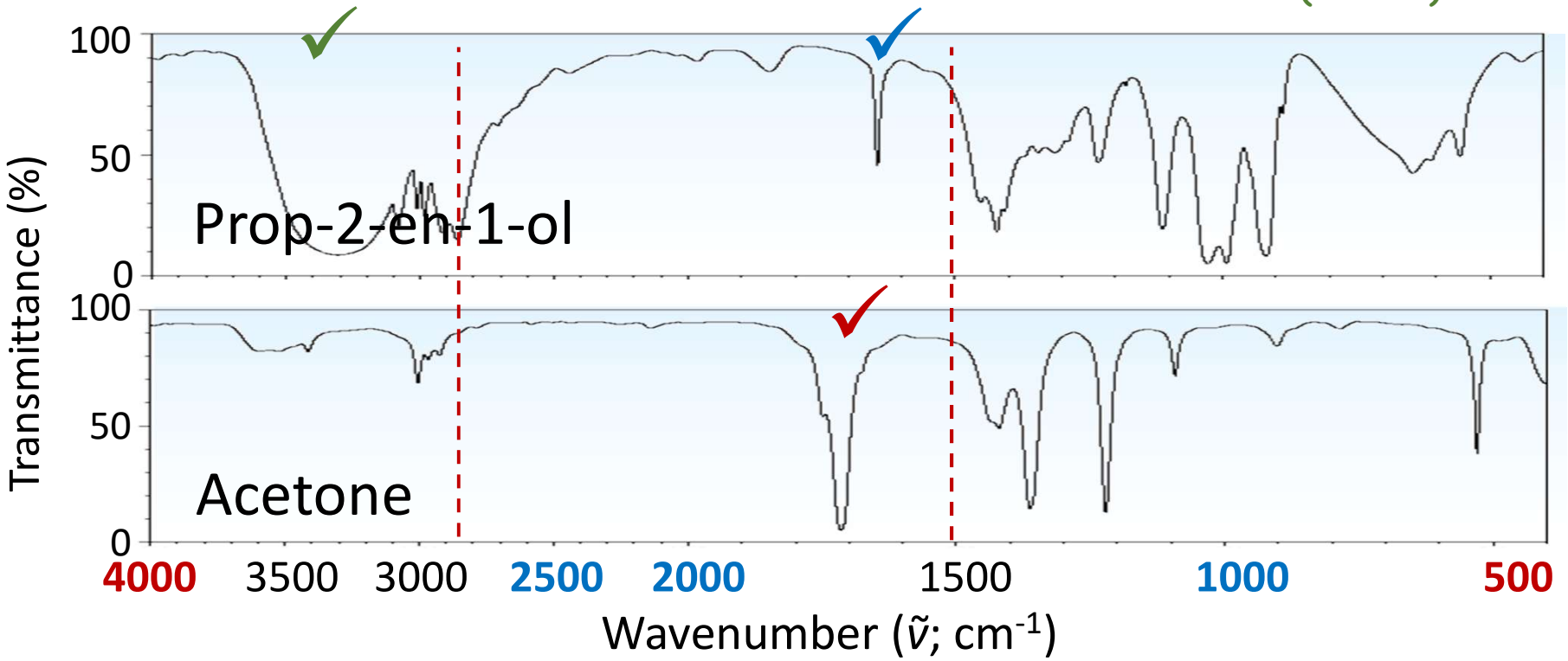


Infrared spectroscopy of alcohols, phenols, aldehydes and ketones

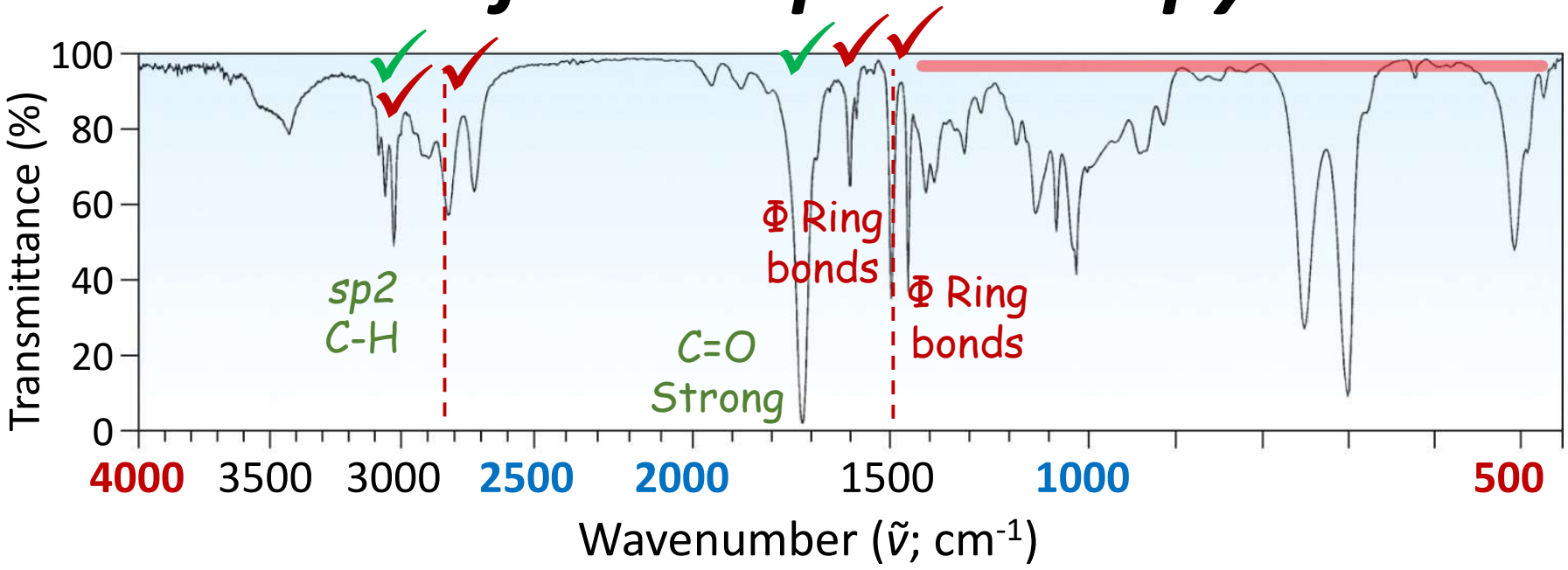


How to use infrared spectroscopy to distinguish two compounds with the same chemical formula C_3H_6O?

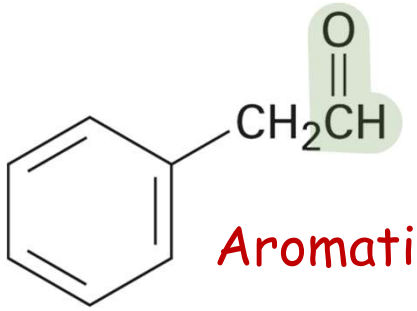
Acetone CH_3COCH_3 1670-1780 *vs* Prop-2-en-1-ol $H_2C=CHCH_2OH$ 1640-1680, 3400-3650 (Broad)



How to predict the structure based on infrared spectroscopy?



The table will be given in my test. Learn how to find the needed info from the table



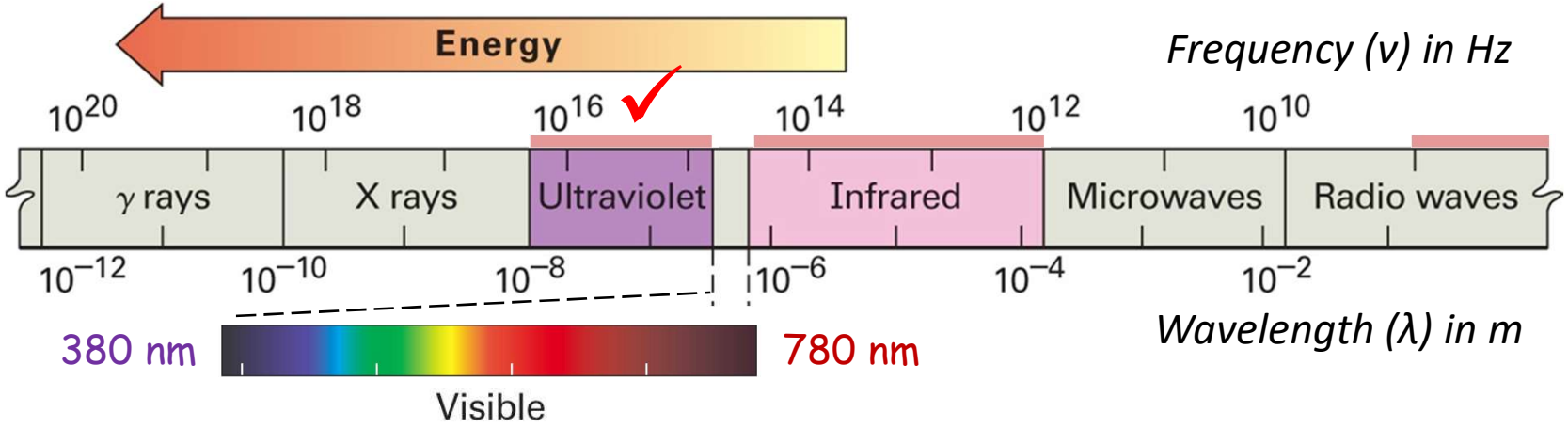
Aldehyde

Aromatic ring

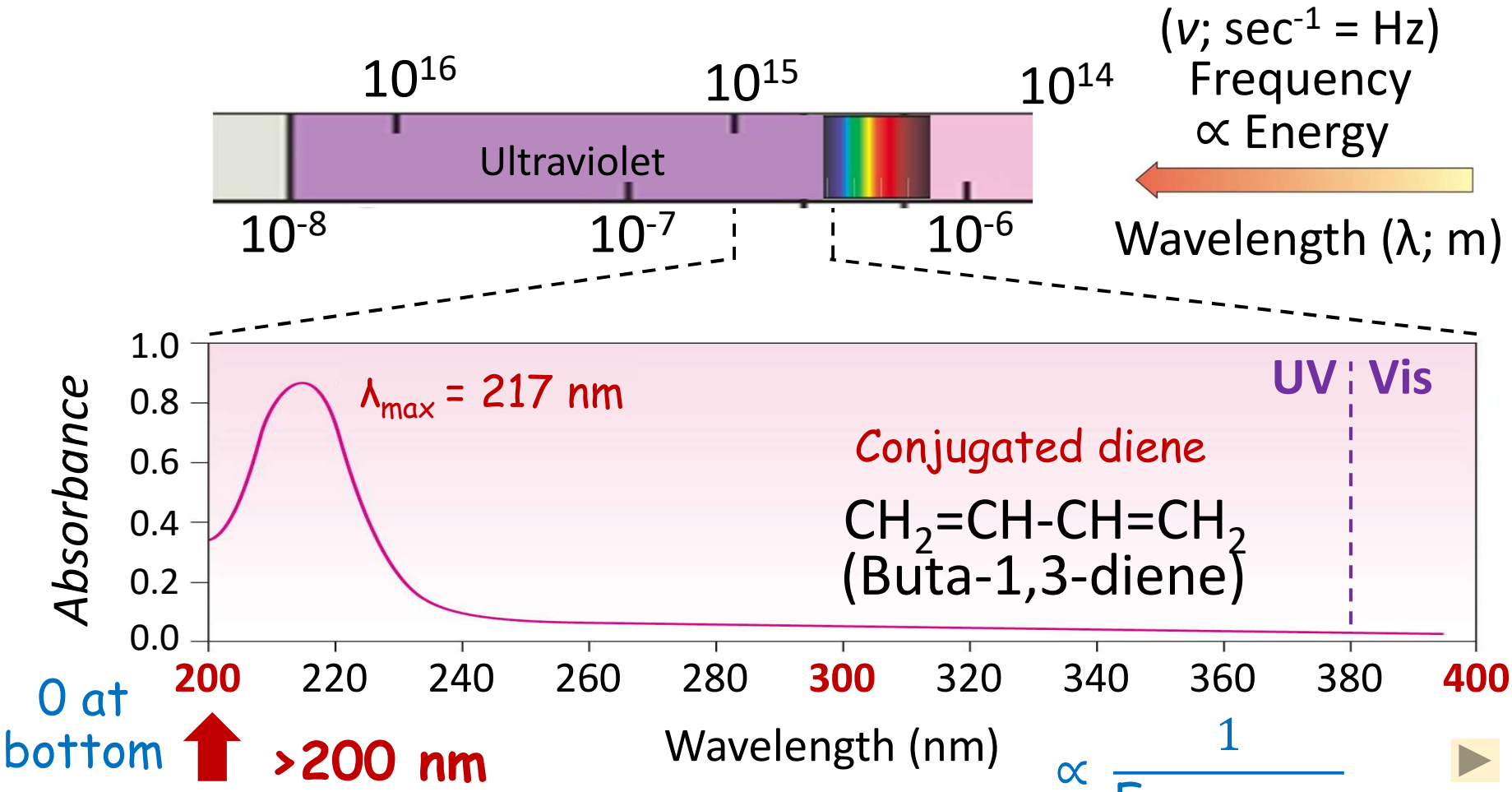
= S2

Spectroscopic analyses of organic compounds

Technique	Electromagnetic radiation	Structure
Infrared spectrometry	Infrared light	Covalent bonds
Ultraviolet spectroscopy	Ultraviolet light	σ–σ^*, n–σ^*, π–π^*, n–π^* transitions
Nuclear magnetic resonance spectroscopy	Radio wave	Atomic nuclei in magnetic field



Ultraviolet spectroscopy



What compounds have a peak in the UV spectrum?

Ultraviolet spectroscopy

- ✓ Ultraviolet spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet spectral regions. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transitions. Absorption spectroscopy measures transitions from the _____state to the _____state.

- ✓ Molecules containing bonding (__and __electrons) or non-bonding electrons (__-electrons) can absorb energy in the form of ultraviolet to excite these electrons to higher anti-bonding molecular orbitals.

Highest Occupied MO

- ✓ The more easily excited the electrons, (*i.e*. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb

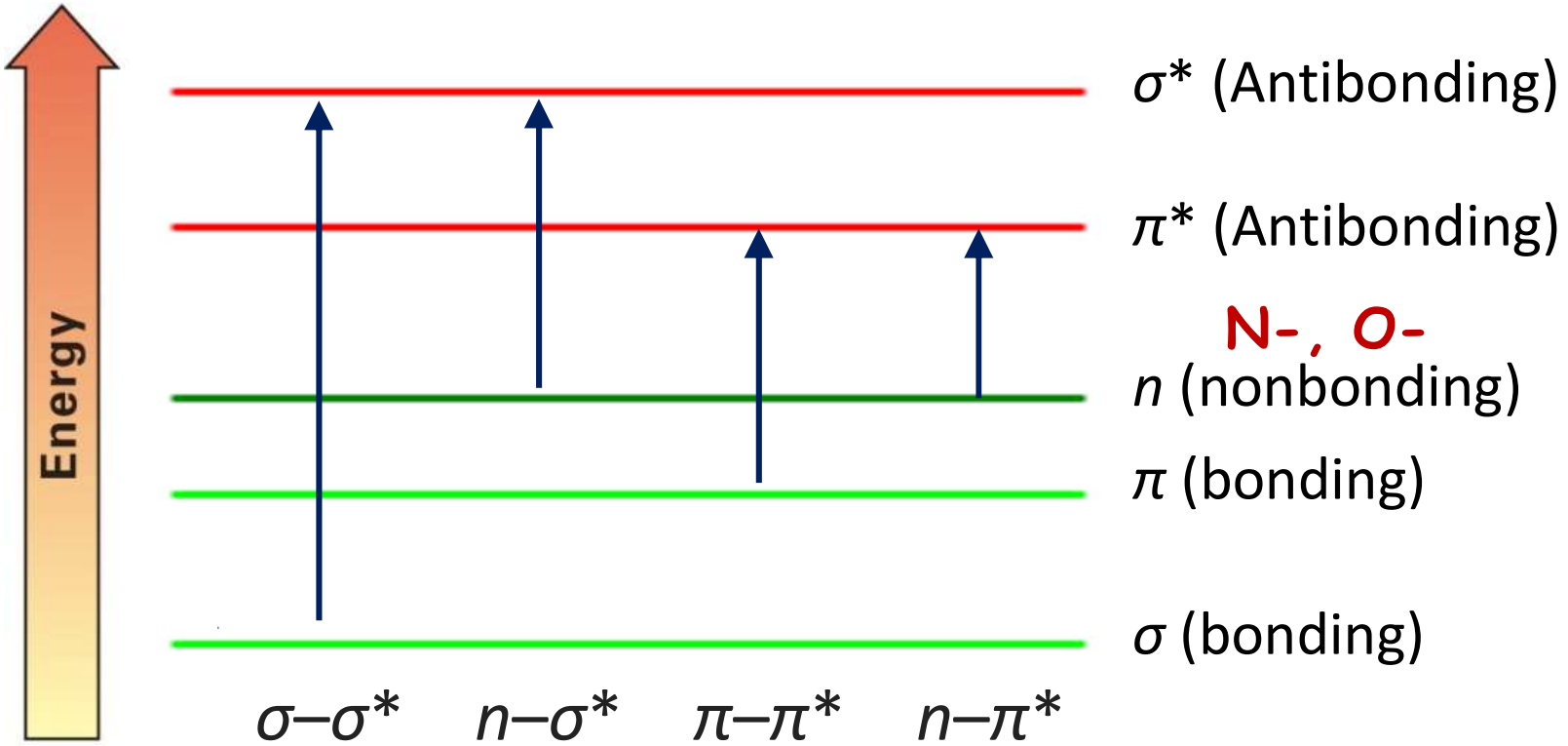
Lowest Unoccupied MO

What properties are examined in UV-Vis?

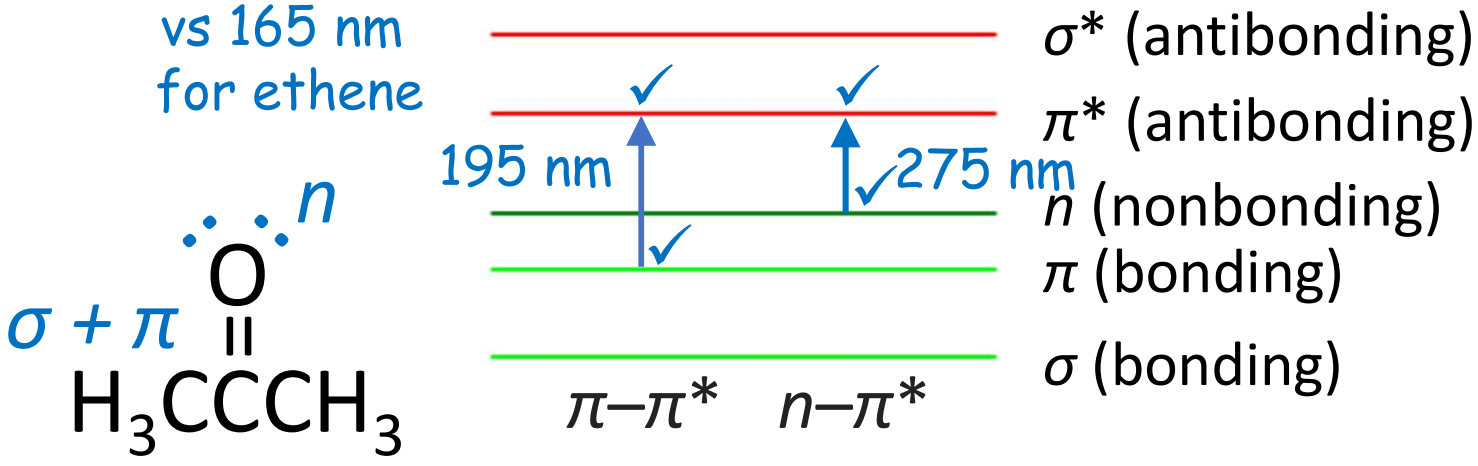
Energy gap between HOMO and LUMO

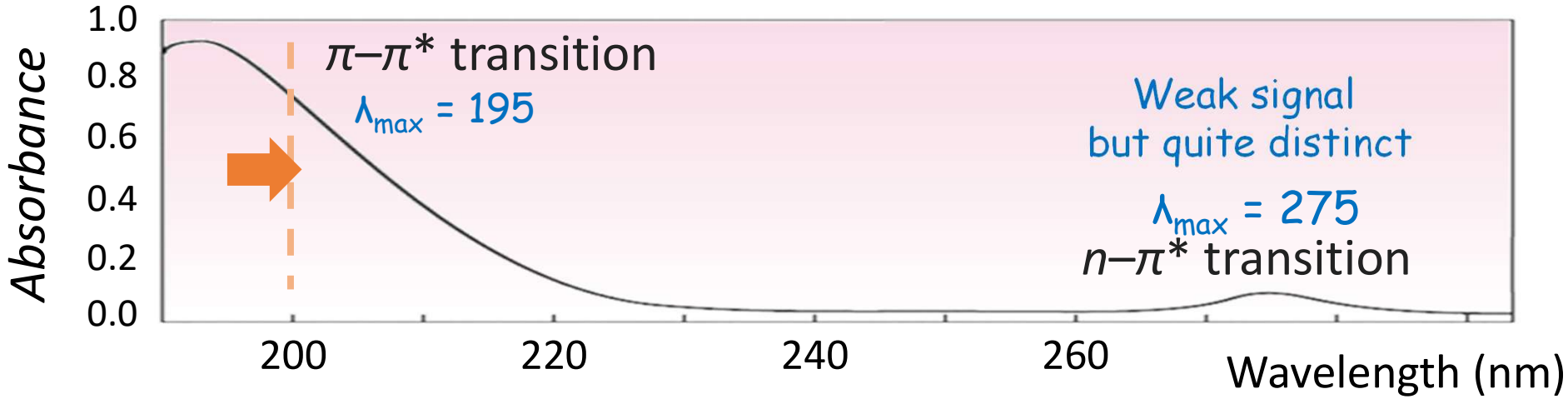
NP5

Various HOMO-LUMO transitions leading to ultraviolet absorption



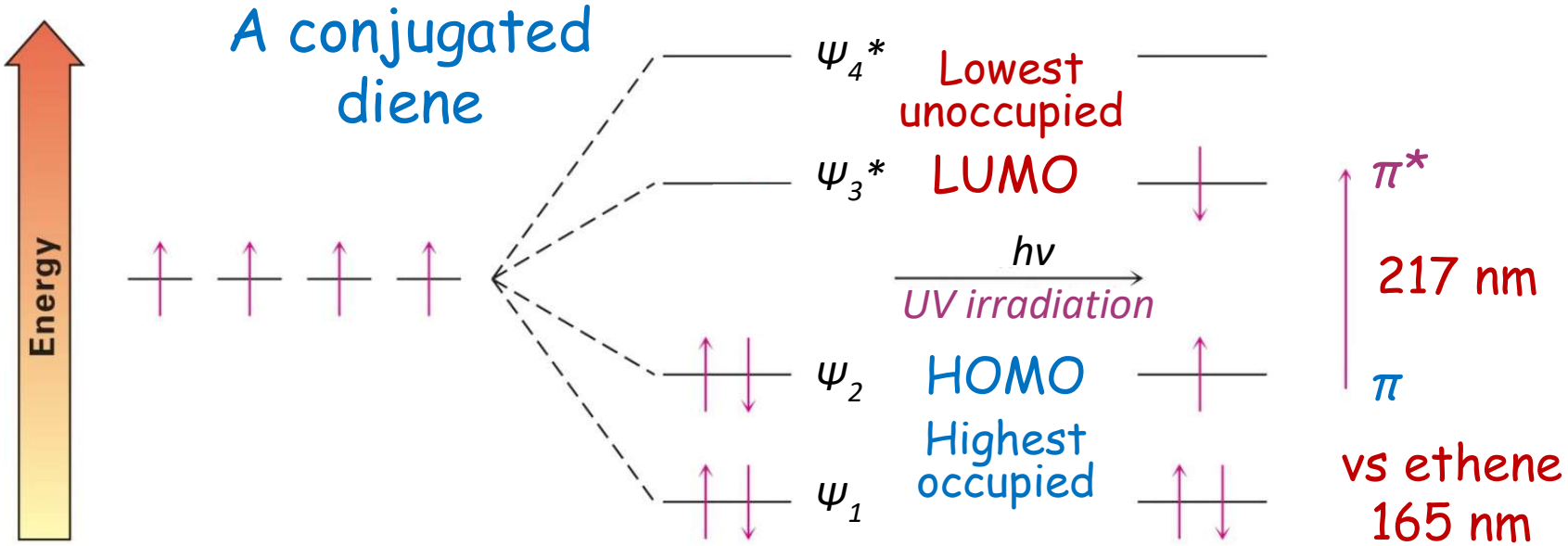
Ultraviolet spectroscopy of acetone





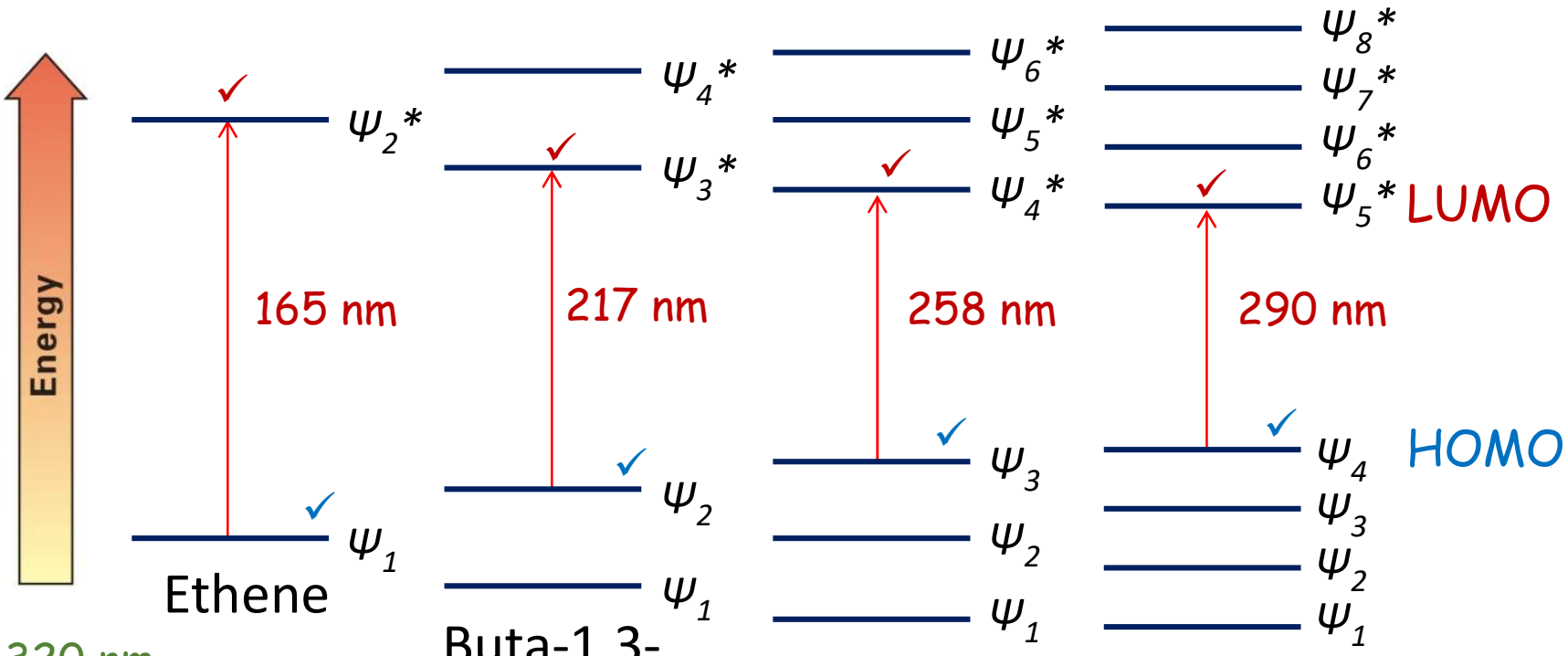
What structure can narrow the energy gap between HOMO and LUMO?

π–π* transition for buta-1,3-diene



Four *2p* atomic orbitals (AO) ⇢ Four Ψ molecular orbitals (MO)

UV absorption in conjugated polyenes



n-π* 320 nm

(219 nm) H_3C | $H_2C{=}CH{-}C{=}O$ E1

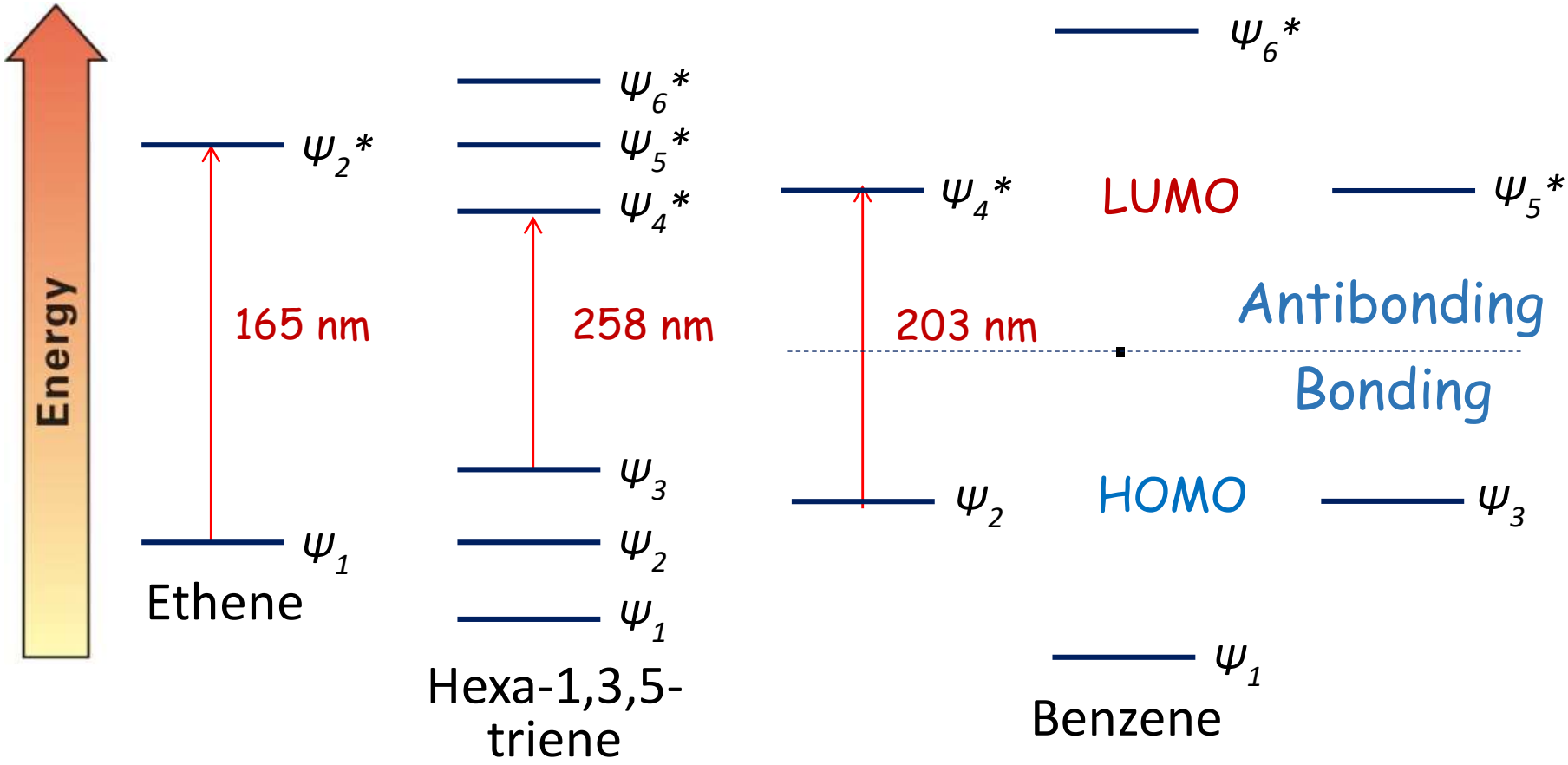
All have similar λ_{max}

(220 nm) H_3C | $H_2C{=}CH{-}C{=}CH_2$

$H_2C{=}CH{-}HC{=}CH_2$ (217 nm)

As the number of _____ C=C becomes higher, the energy gap between HOMO and LUMO decreases and the wavelength of absorbed light _____

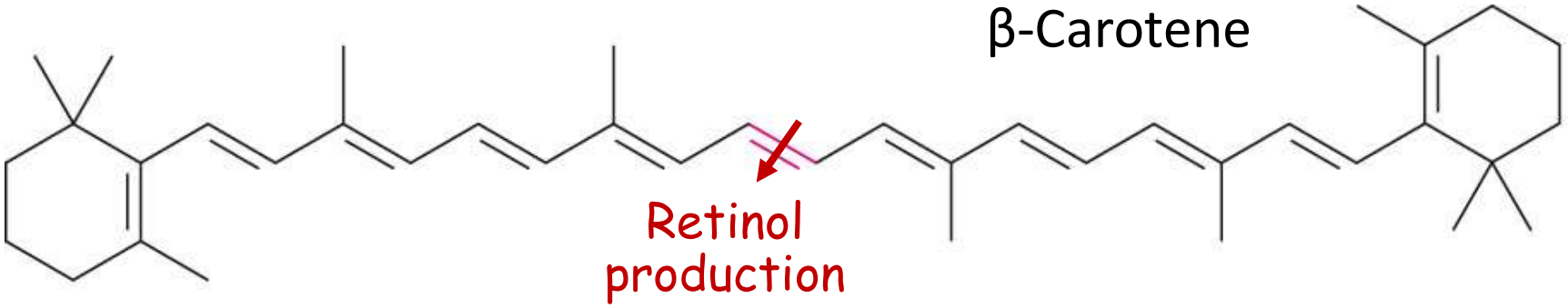
UV absorption in cyclic vs linear conjugation



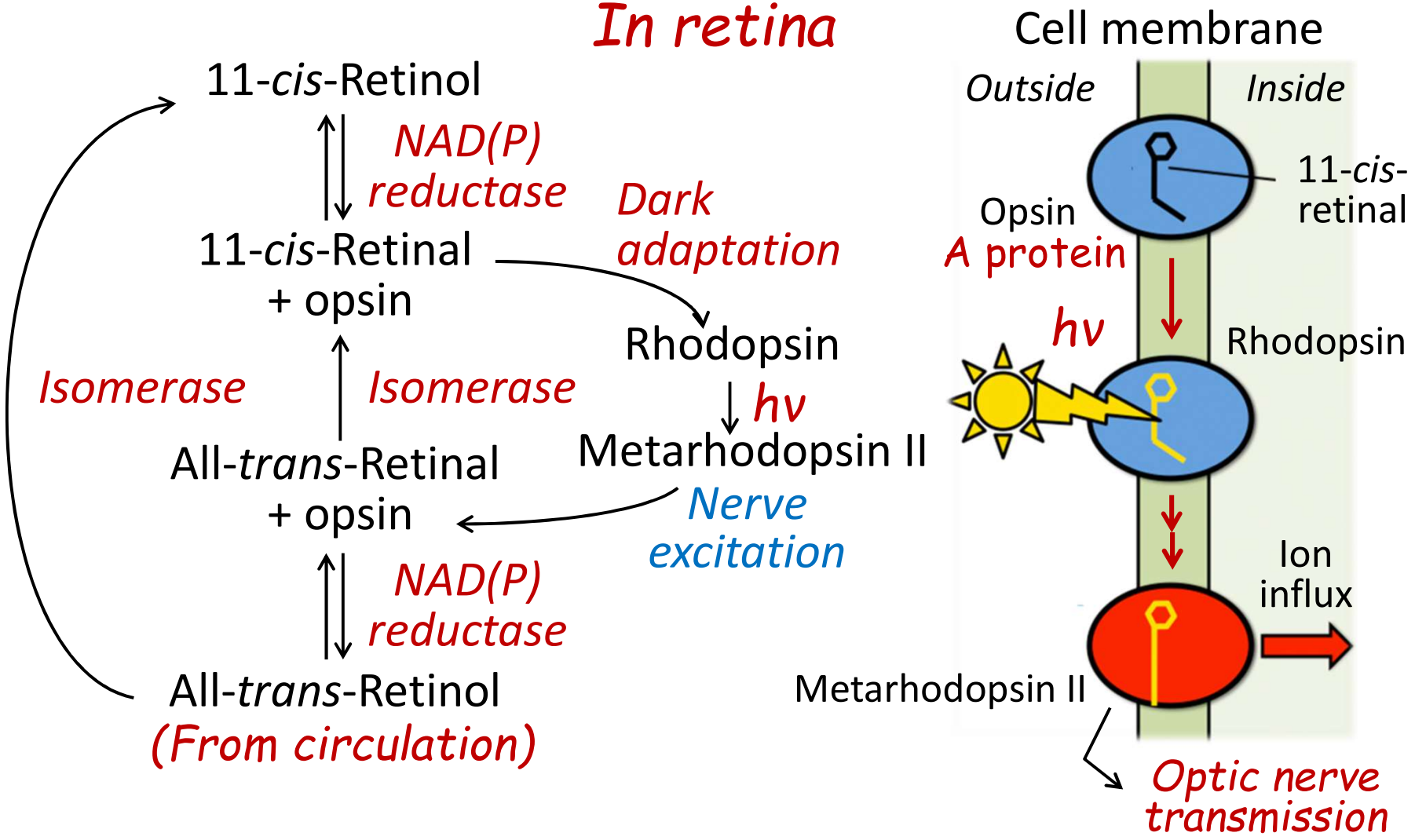
Cyclic conjugation may give a peak with $\lambda_{max} > 200$ nm in UV spectra as well

Colors of organic compounds result from extensive conjugation

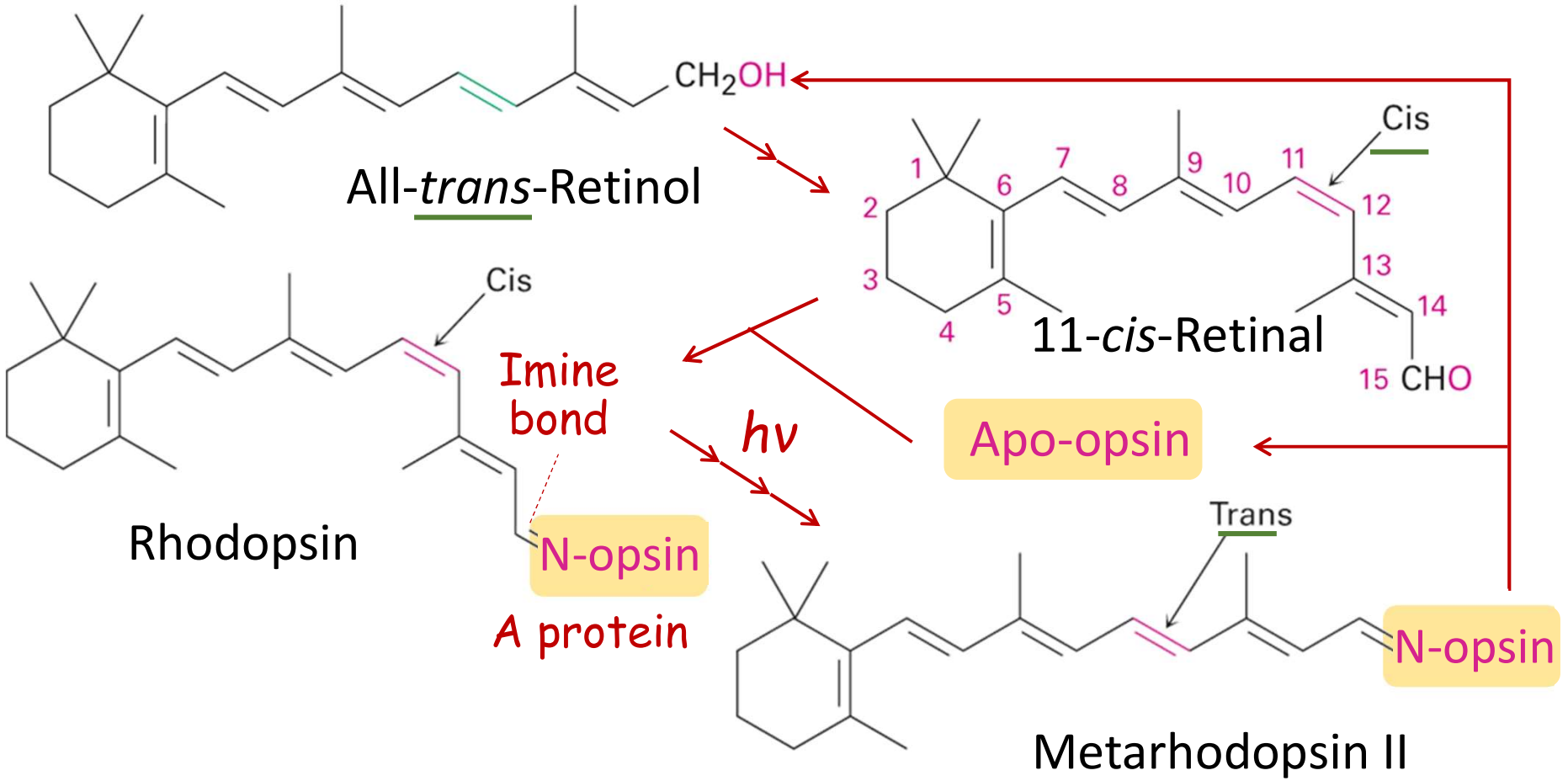
- ✓ As the number of conjugated C=C becomes higher, the energy gap between HOMO and LUMO decreases. When the wavelength of absorbed light is in the range of visible light, the compound should become colored
- ✓ β-Carotene has λ_{max} = 455 nm. When white light strikes β-carotene, wavelengths in the blue region are absorbed. Thus, the yellow-orange colors are transmitted to our eyes



A vitamers in visual cycle



Some structures in visual cycle



Absorbance (A) and molar absorptivity (ε)

Absorbance (A) is the common logarithm of the ratio of incident (I_0) to transmitted (I) radiant power through a material

$$A = \log \frac{I_0}{I}$$

Molar absorptivity (ε), or molar extinction coefficient, is a measure of how strongly a chemical species or substance absorbs light at a particular wavelength

$$\varepsilon = \frac{A}{\mathbf{c}L} \; ; \; \mathbf{c} = \frac{A}{\varepsilon L}$$

Molar concentration

Sample pathlength (cm)