CHEM 103: Chemistry in Context

Unit 4.1

Atmospheric Chemistry:
the ozone layer

Reading: Chapter 2

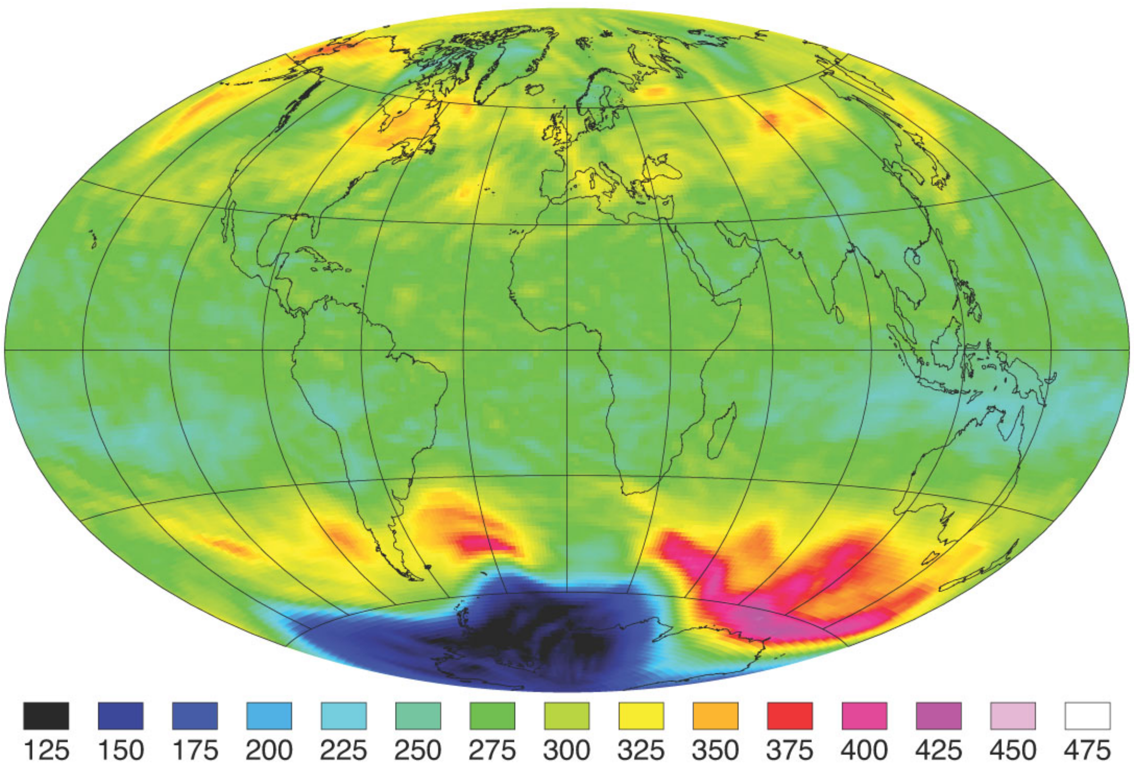
Colorado State University

Unit 4.1 Plan

- What is ozone and where does it come from?
  - allotropes (same element, different forms)
  - molecular structure
  - What does (UV) light do to us and how does ozone play a role?
  - light as radiant energy
  - interaction between UV light and ozone
  - biological impact of UV light
- Ozone depletion in the stratosphere and our response…
  - halogens and chlorofluorocarbons (CFCs)
  - social change (positive) resulting from widespread use of CFCs
  - atmospheric change (negative) resulting from widespread use of CFCs
  - replacements for CFCs

The Ozone "Layer"

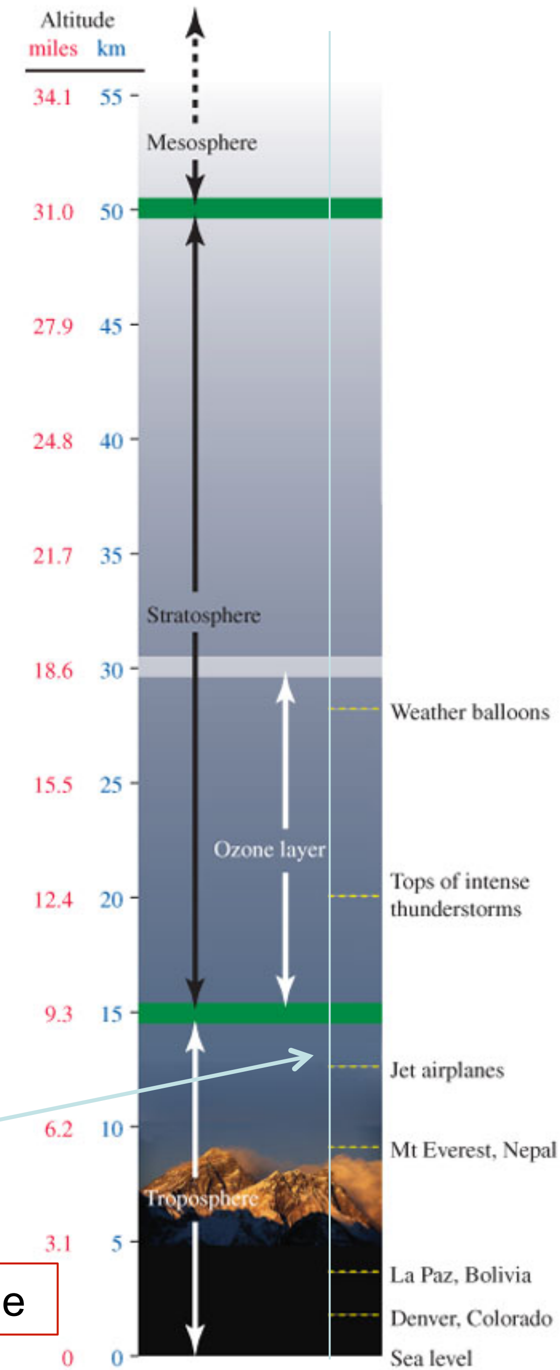
Total Ozone on September 25, 2006



1 Dobson Unit (DU): 3×10^{16} molecules of ozone in a column of air with cross section 1 cm^2

- measured by measuring how much UV light is blocked in a column of air

1 DU ~ 1 ppb ozone

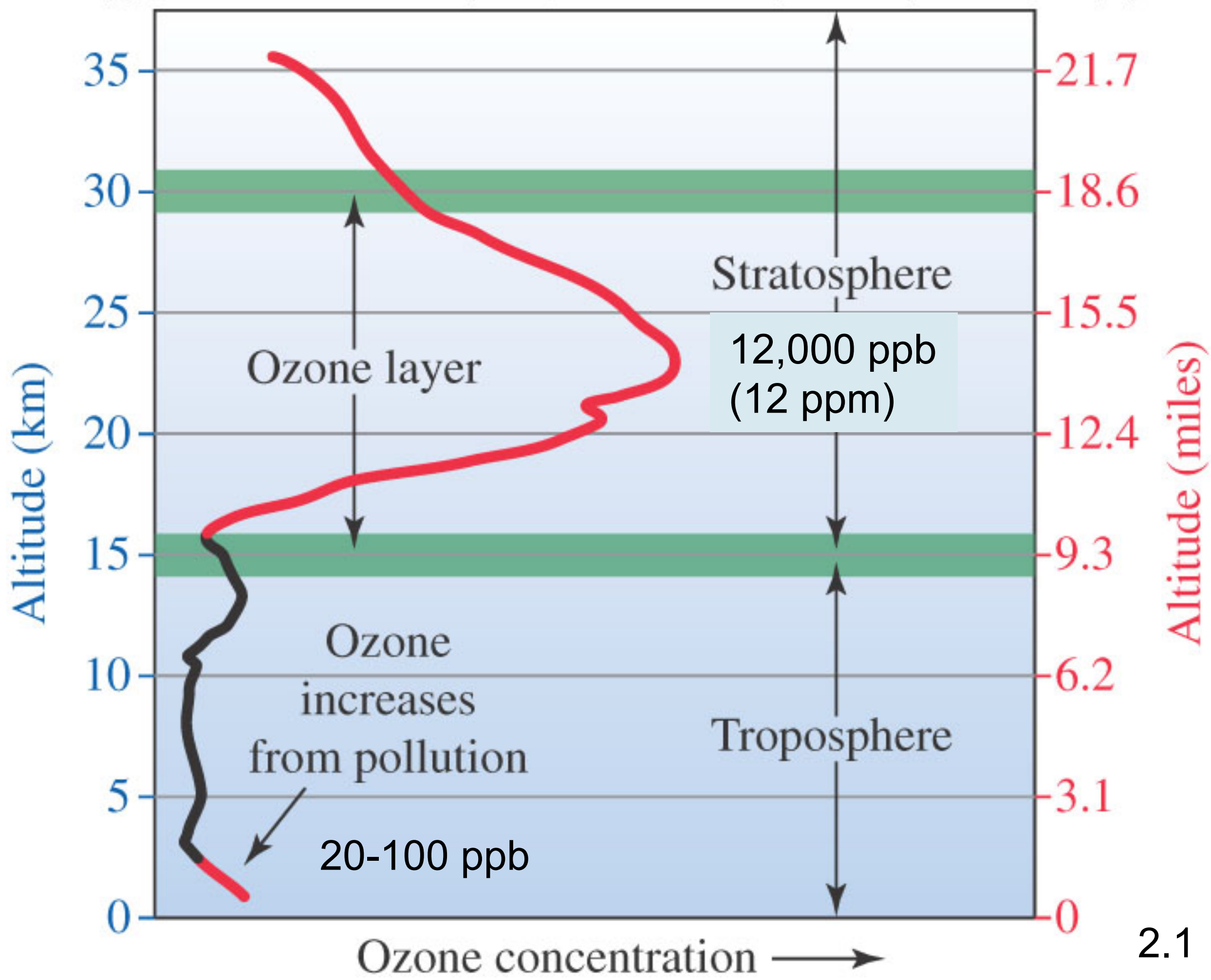


Ozone: What and Where is It?

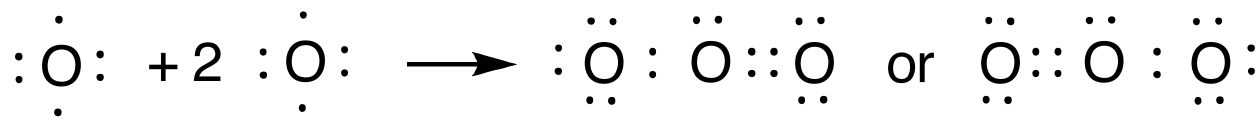
energy + $3O_2 \rightarrow 2O_3$ Ozone

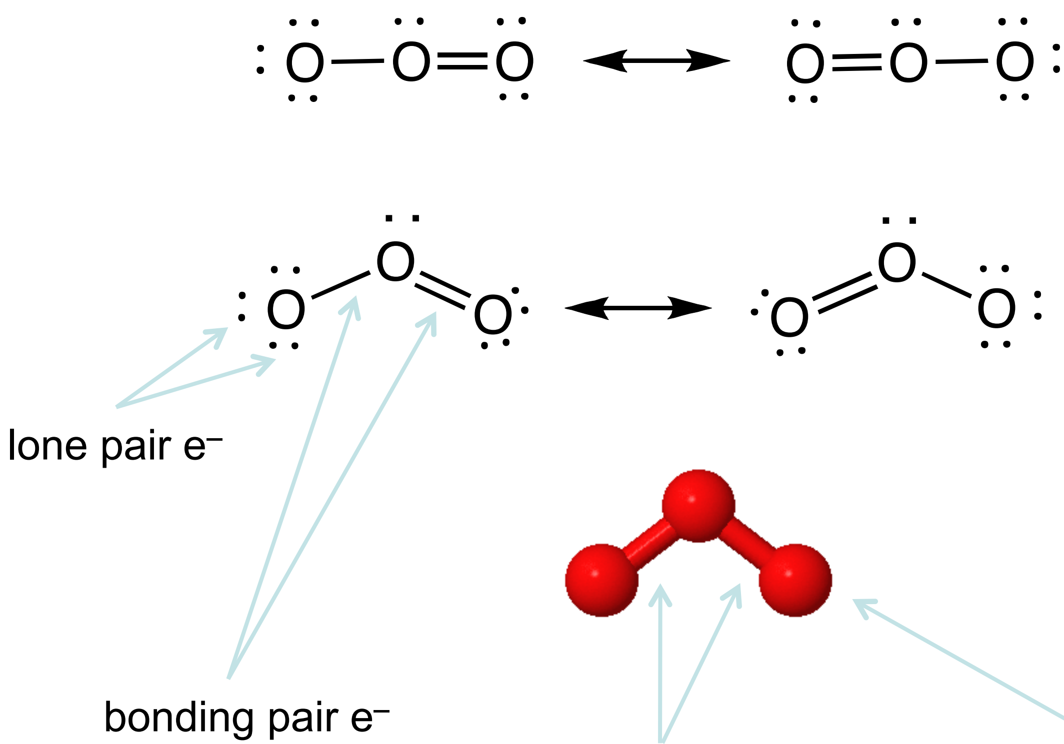
Ozone is an **allotrope** of oxygen: different forms of same element with differing structures & hence differing properties

National Ambient Air Quality Standards (troposphere):
0.12 ppm for 1-hr average
0.08 ppm for 8-hr average
(see table 1.5)



Ozone, O_3



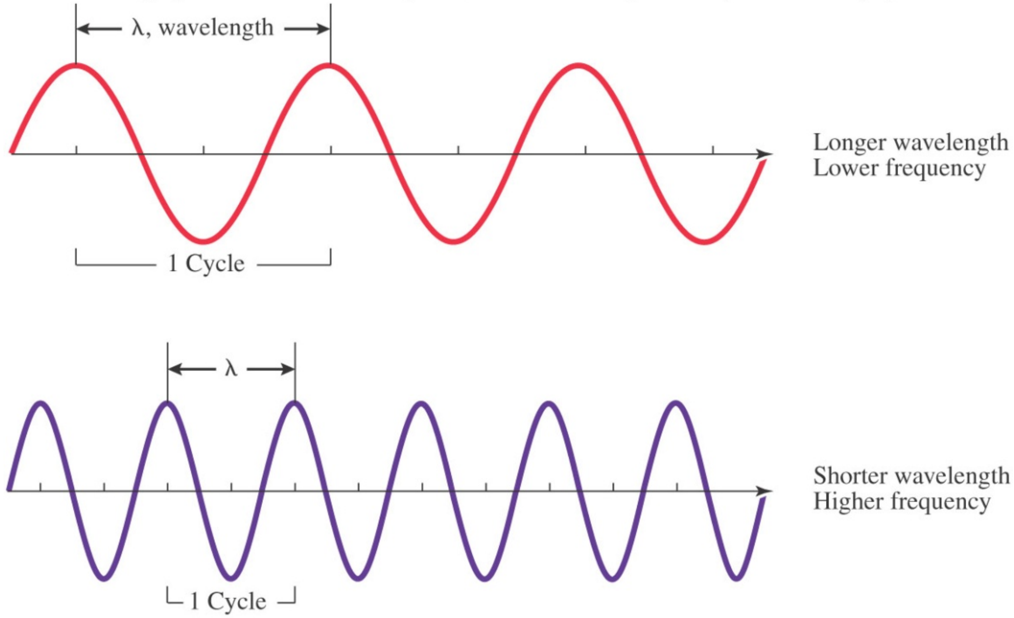


double arrow indicates **resonance structures**—the “true” structure is a combination of the canonical resonance structures

true structure: both O-O distances are the same

true shape: ozone is bent, just like water

Review of Waves



wavelength (λ): distance covered in one cycle
(peak-to-peak or trough-to-trough)

frequency (v): number of cycles per unit time
Hertz (Hz) = #cycles/second

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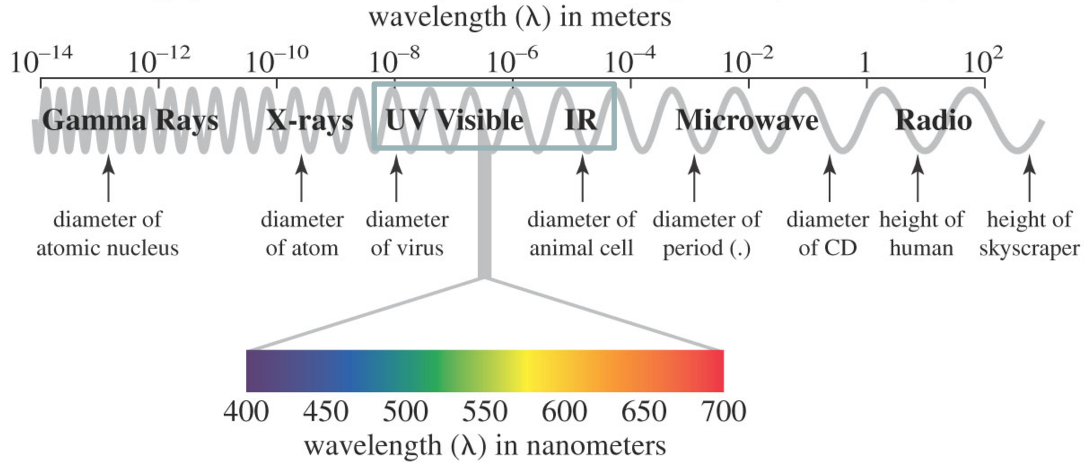
$$\text{frequency } (\nu) = \frac{\text{speed of light}(c)}{\text{wavelength}(\lambda)} \Rightarrow \nu\lambda = c \text{ (a constant) as } \lambda \uparrow, \nu \downarrow$$

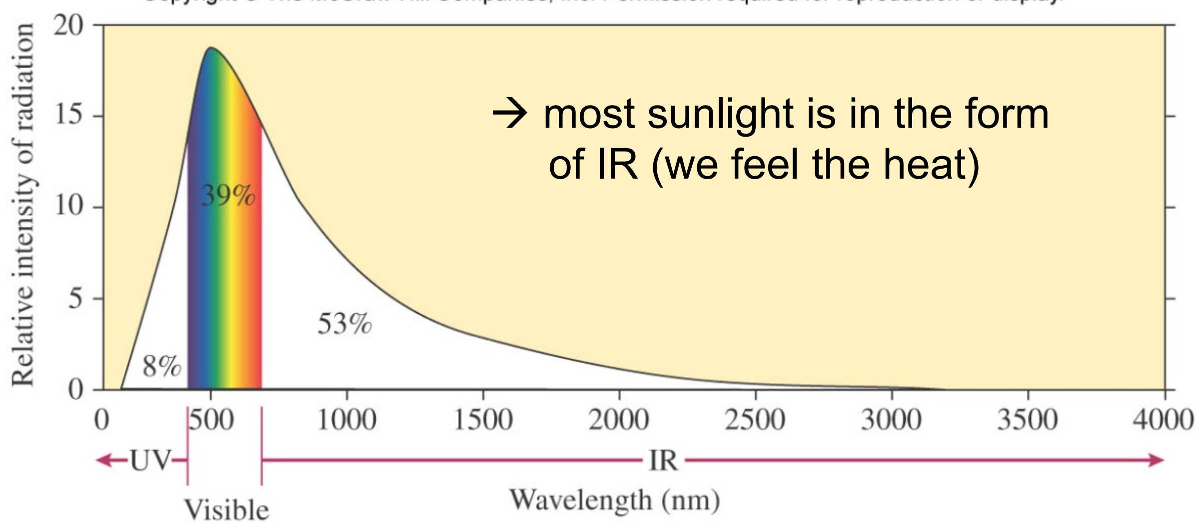
note: $c = 3 \times 10^8$ m/s

Light: a Subset of Radiant Energy

Electromagnetic spectrum:

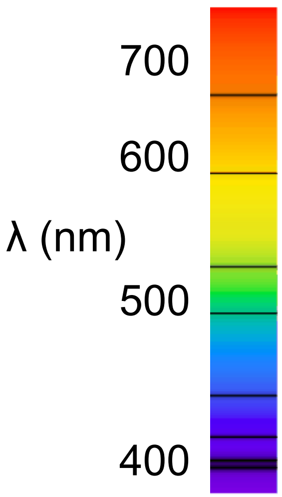


Output from the sun:



→ most sunlight is in the form of IR (we feel the heat)

UV-Visible Spectrum



versus

gov't officials didn't take CHEM 103…

TABLE 11-1
Visible light and complementary colors

Wavelength range (nm)	*Wave numbers (cm^{-1})*	*Color*	*Complementary color*
< 400	> 25,000	ultraviolet	
400-450	22,000-25,000	violet	yellow
450-490	20,000-22,000	blue	orange
490-550	18,000-20,000	green	red
550-580	17,000-18,000	yellow	violet
580-650	15,000-17,000	orange	blue
650-700	14,000-15,000	red	green
> 700	< 14,000	infrared	

Light: Waves/Particles of Radiant Energy

"Dual" nature of light:

1. wave properties (λ,v)
--two light beams don't interfere with each other

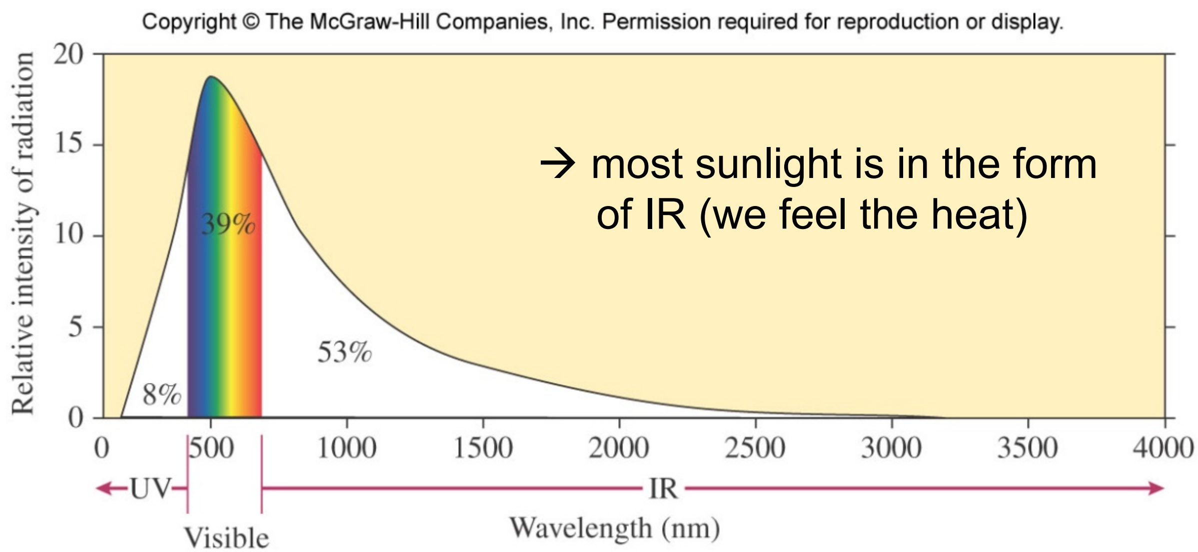
2. particle properties
--energies of light are quantized (while a wave is continuous), leading to photons: "packets" of radiation

Energy (E) = hc/λ

h = Planck's constant
c = speed of light

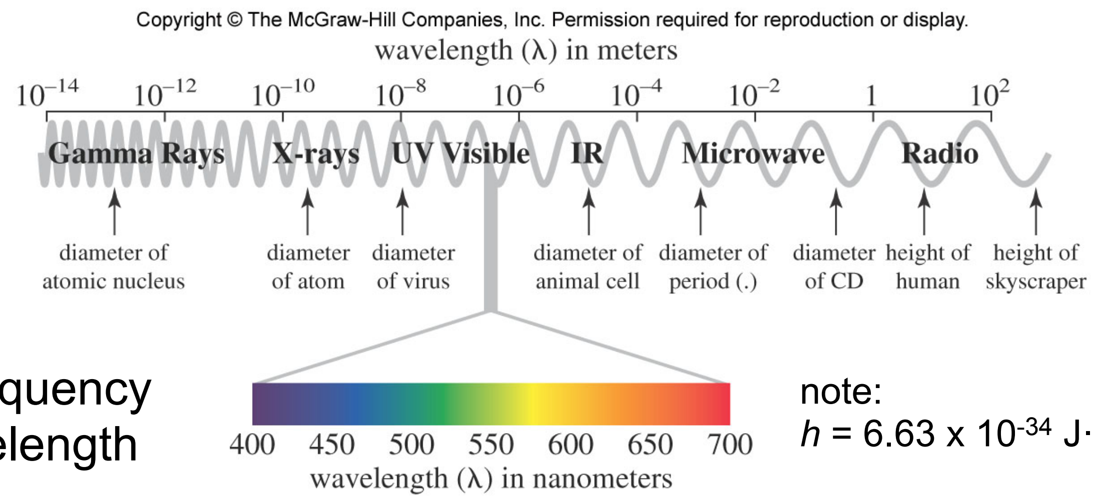
remember: $v = c/\lambda$
therefore: E = hv

Thus, energy is proportional to frequency and inversely proportional to wavelength



High energy: small λ, high v

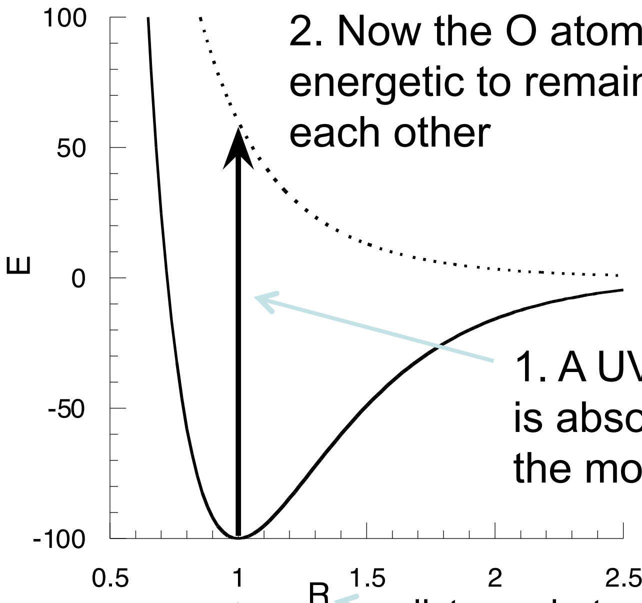
Low energy: large λ, low v



note:
$h = 6.63 \times 10^{-34}$ J·s

Using Light to Break Bonds

Potential energy diagram:

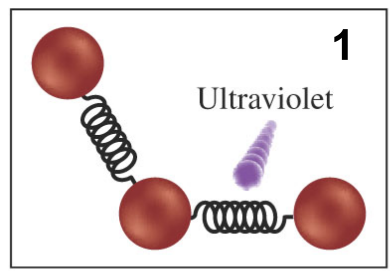


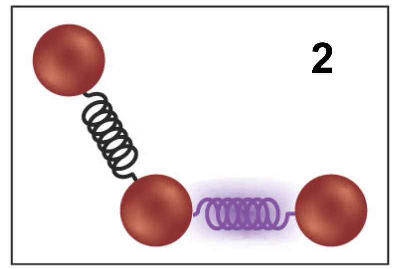
2. Now the O atoms are too energetic to remain close to each other

1. A UV photon is absorbed by the molecule

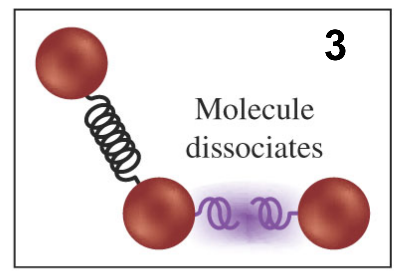
distance between O atoms

A stable molecule has an equilibrium O-O distance

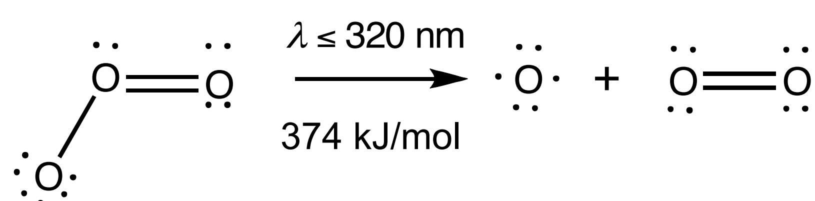




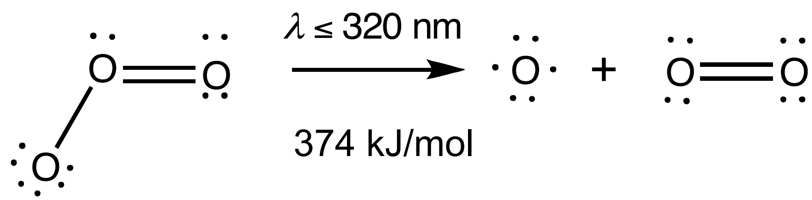
3. O-O bond breaks



Net process:



Using Light to Break Bonds



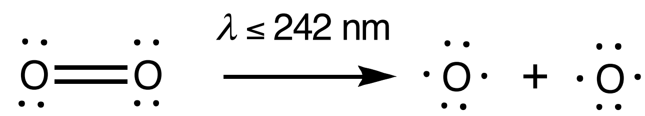


Table 4.2 Bond Energies (in kJ/mol)

	H	C	N	O	S	F	Cl	Br	I
Single Bonds									
H	436								
C	416	356							
N	391	285	160						
O	467	336	201	146					
S	347	272	—	—	226				
F	566	485	272	190	326	158			
Cl	431	327	193	205	255	255	242		
Br	366	285	—	234	213	—	217	193	
I	299	213	—	201	—	—	209	180	151

Multiple Bonds

C=C	598	C=N	616	C=O	803 in CO_2
C≡C	813	C≡N	866	C≡O	1073
N=N	418	O=O	498		
N≡N	946				

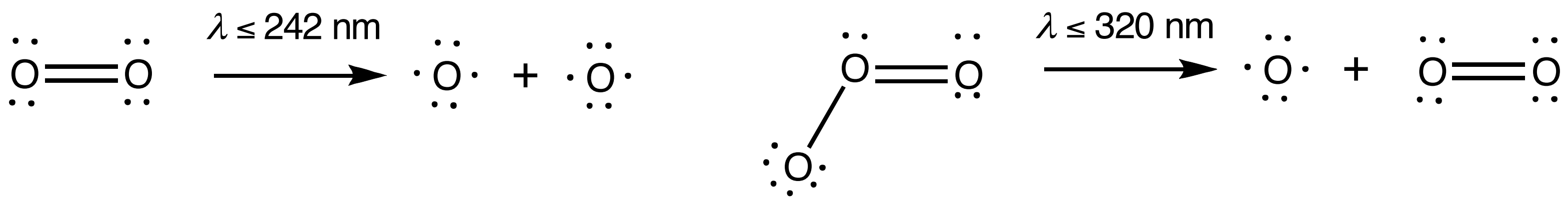
Source: Data from Darrell D. Ebbing, *General Chemistry,* Fourth Edition, 1993 Houghton Mifflin Co. Data originally from *Inorganic Chemistry: Principles of Structure and Reactivity,* Third Edition, by James E. Huheey, 1983, Addison Wesley Longman.

More energy is required to break O-O bonds in oxygen than in ozone…

Types of UV Light and Chemical/Biological Effects

Table 2.4 Categories and Characteristics of UV Radiation

Radiation	Wavelength Range (nm)	Relative Energy	Comments
UV-A	320–400	Least energetic of these three UV categories	Least damaging, reaches Earth's surface in greatest amount
UV-B	280–320	More energetic than UV-A, less energetic than UV-C	More damaging than UV-A, less damaging than UV-C, most absorbed by O_3 in the stratosphere
UV-C	200–280	Most energetic of these three categories	Most damaging of these three, but not a problem because totally absorbed by O_2 and O_3 in stratosphere



Biological Impact of UV Radiation

In addition to breaking O-O bonds in O_2 and O_3, UV radiation can break other bonds…

Biological sensitivity measures the impact on DNA, our formula tape for who we are. Mistakes can lead to cancer, birth defects …

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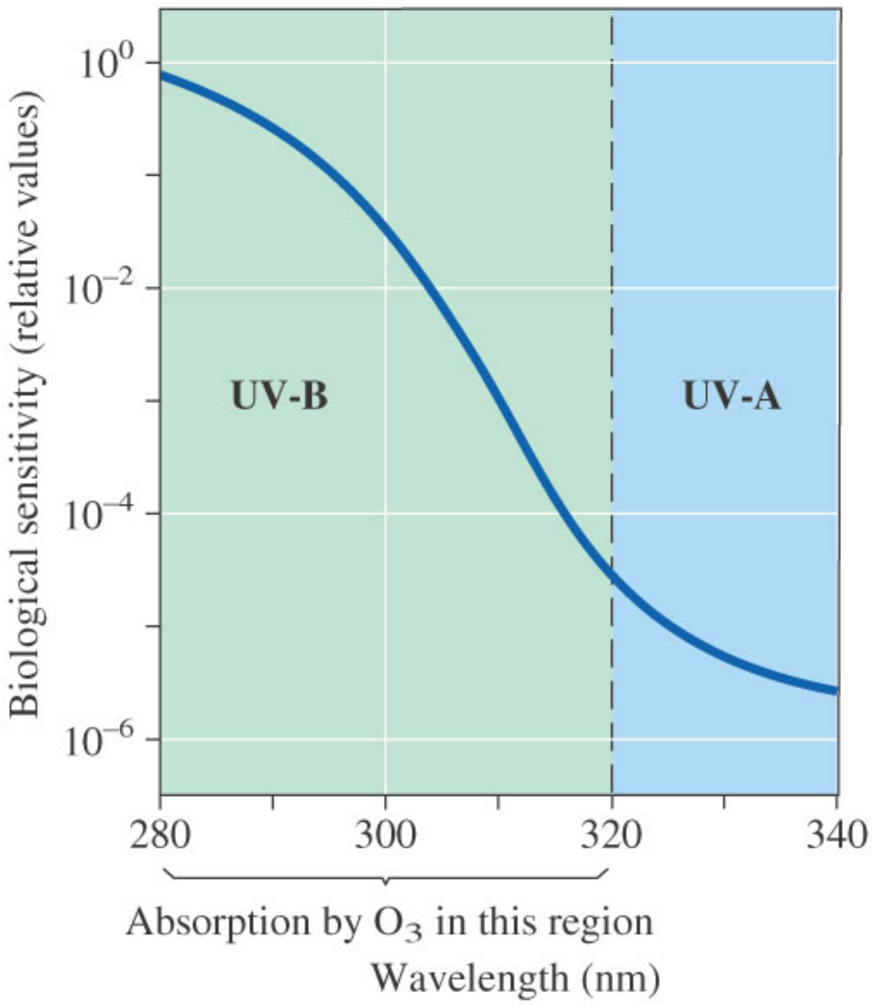
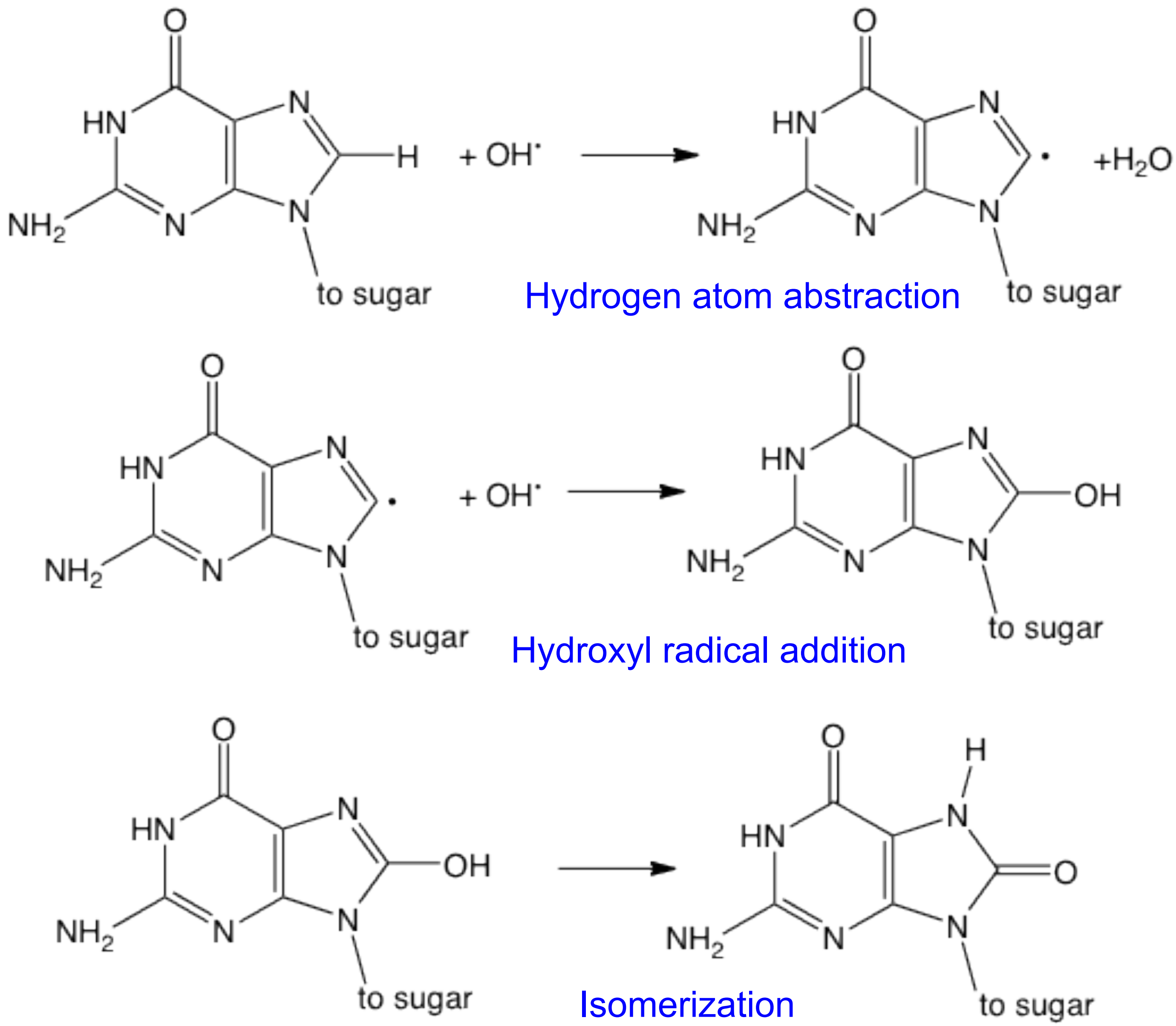
374 kJ/mol

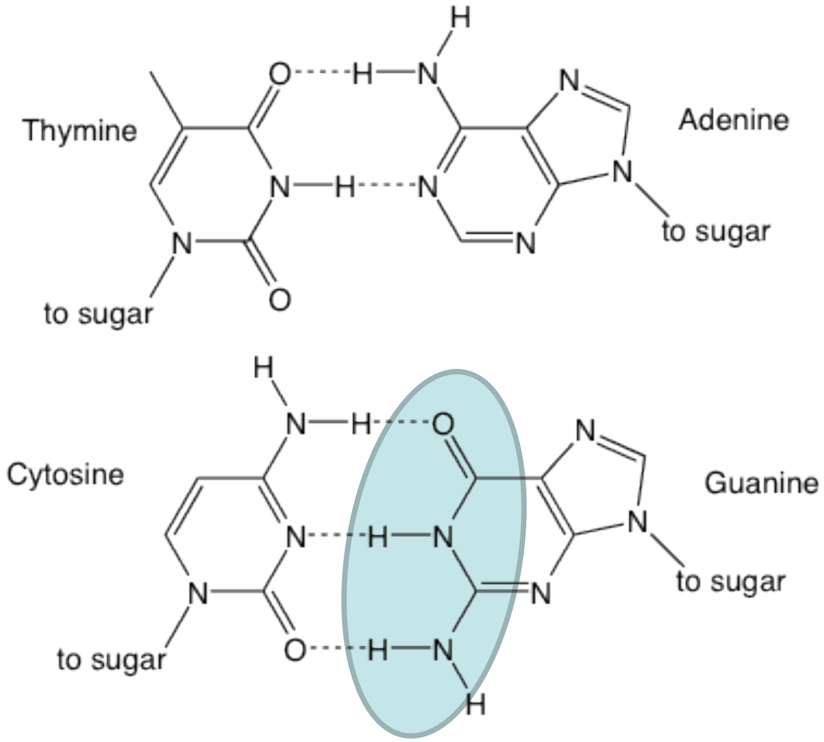


Consequence of ROS Production: Guanine Oxidation

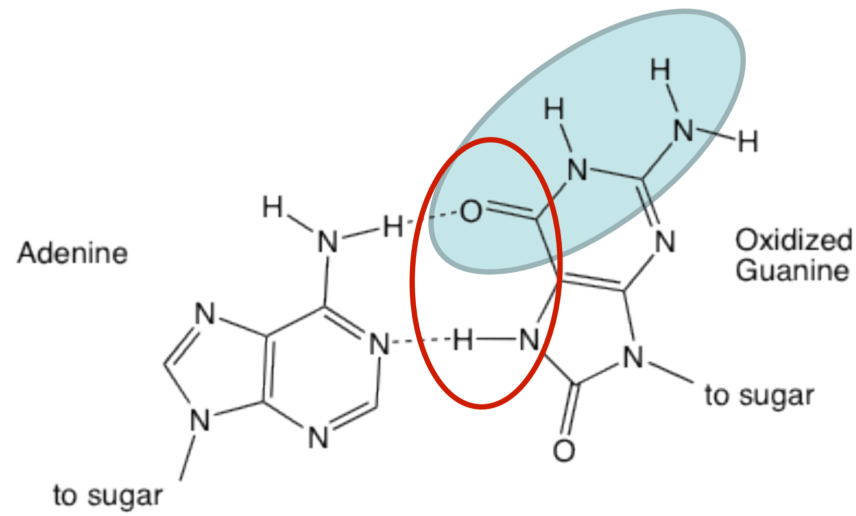


Guanine Oxidation Leads to Base-Pairing Disruption

Normal base-pairing



Mismatched base-pairing
Instead of A-T we now have
A-G



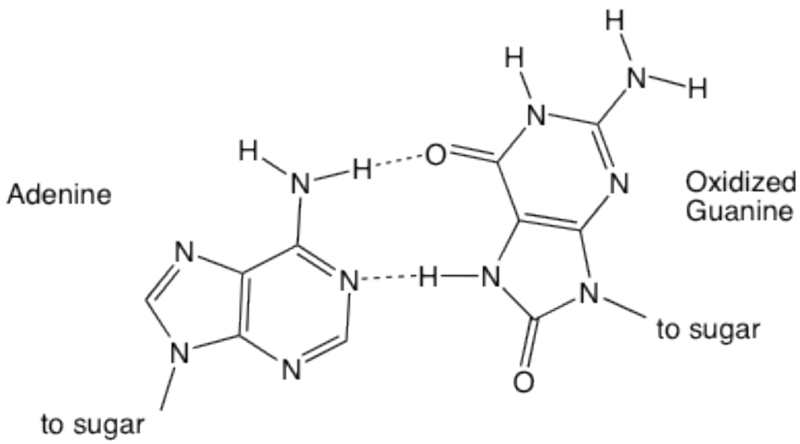
T – A
C – G

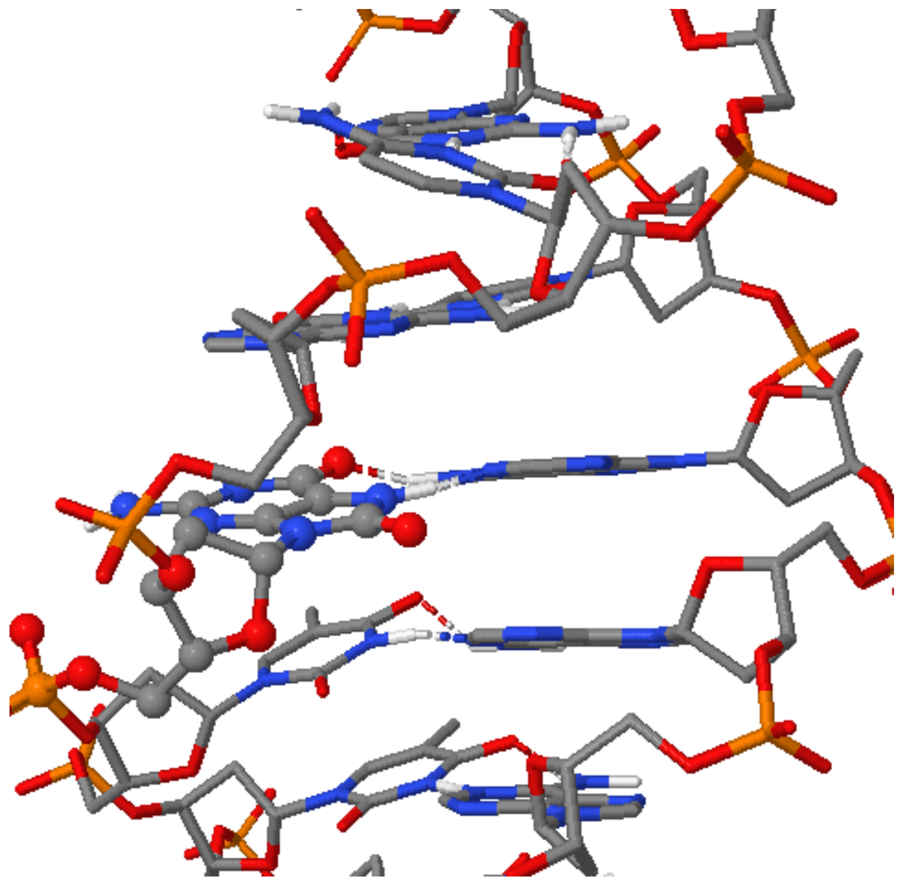
critical to proper DNA replication and transcription

A – G

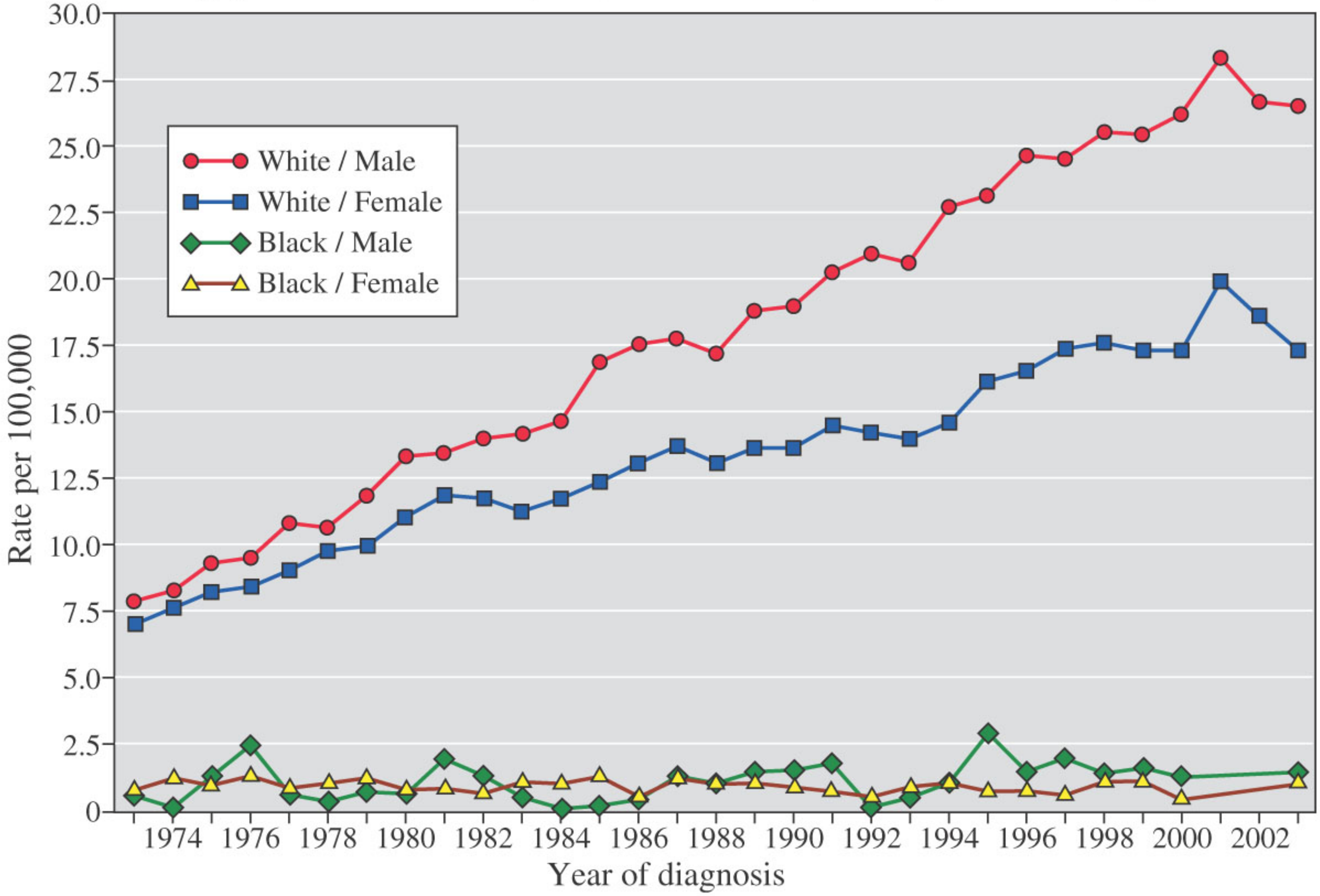
Rutroh Astro…

DNA Duplex with Oxidized Guanine





Incidence of Melanoma in US

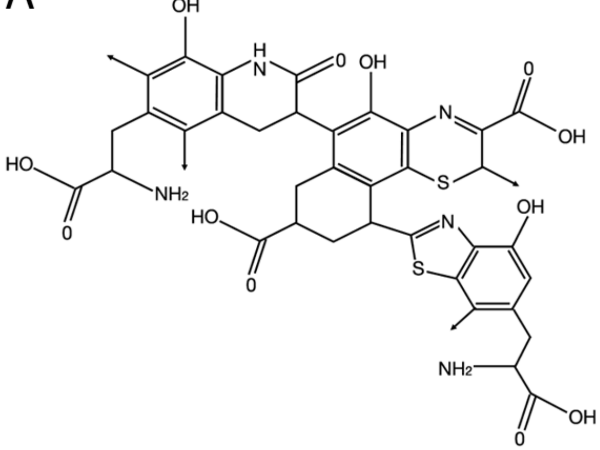


Tanning Beds

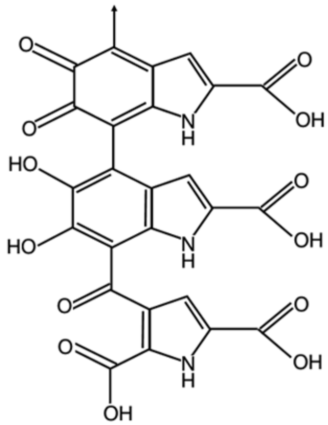
Use both UV-A & UV-B radiation
Exposure leads to melanin production

New Jersey Mom

A



B



Molecular **structure** of phaeomelanin (A) and eumelanin (B)

Sunscreens

Sunscreens absorb and/or scatter UVA & UVB radiation

© Courtesy Blue Lizard Products

Note: the Sun Protection Factor (SPF) only measures blockage of UVB light

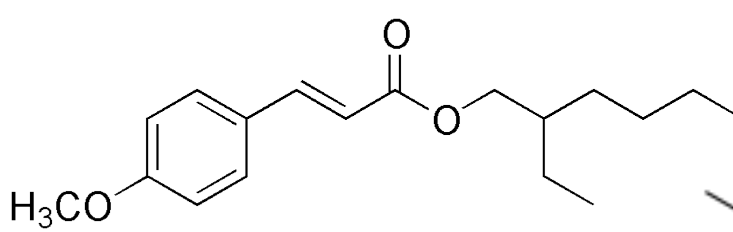
TiO_2 & ZnO **scatter** UV light

Table 2.5 The UV Index

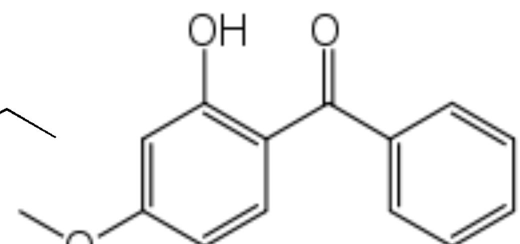
Exposure Category	Index	Sun Protection Messages
LOW	<2	Wear sunglasses on bright days. In winter, reflection off snow can nearly double UV strength. If you burn easily, cover up and use sunscreen SPF 15+.
MODERATE	3–5	Take precautions, such as covering up and using sunscreen SPF 15+, if you will be outside. Stay in shade near midday when the Sun is strongest.
HIGH	6–7	Protection against sunburn is needed. Reduce time in the Sun between 10 AM and 4 PM. Cover up, wear a hat and sunglasses, and use sunscreen SPF 15+.
VERY HIGH	8–10	Take extra precautions. Unprotected skin will be damaged and can burn quickly. Try to avoid the Sun between 10 AM and 4 PM. Otherwise, seek shade, cover up, wear a hat and sunglasses, and use sunscreen SPF 15+.
EXTREME	11+	Take all precautions. Unprotected skin can burn in minutes. Beachgoers should know that white sand and other bright surfaces reflect UV and will increase UV exposure. Avoid the Sun between 10 AM and 4 PM. Seek shade, cover up, wear a hat and sunglasses, and use sunscreen SPF 15+.

Source: The Environmental Protection Agency, 2006.

These organic molecules **absorb** UV light & emit IR radiation:



octyl methoxycinnamate (OMC)



oxybenzone