UNIVERSITÉ Concordia UNIVERSITY

CHEM 333

INTRODUCTION TO QUANTUM THEORY

PROBLEM SET I – SOLUTION KEY

1. The force constant of O_2 is 1140 $N.m^{-1}$. Assuming a harmonic oscillator model for the vibrational motion of O_2, what are the diatomic vibrational frequency and wavenumber?

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_O m_O}{m_O + m_O} = \frac{m_O}{2} = \frac{1}{2}\cdot 16g/mol \cdot \frac{10^{-3}kg}{1g}\cdot\frac{1mol}{6.02\cdot 10^{23}} = 1.3289\cdot 10^{-26}kg$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{1140Nm^{-1}}{1.3289\cdot 10^{-26}kg}} = 4.66\cdot 10^{13}s^{-1}$$

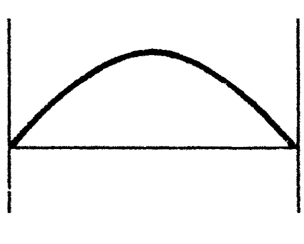
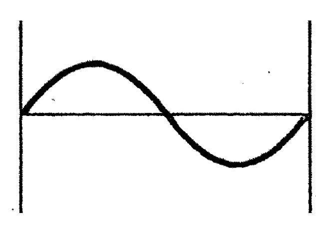
wavenumber: $$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{4.66\cdot 10^{13}s^{-1}}{2.9989\cdot 10^{10}cms^{-1}} = 1556\ cm^{-1}$$

2. Consider a wave made of the first two harmonics

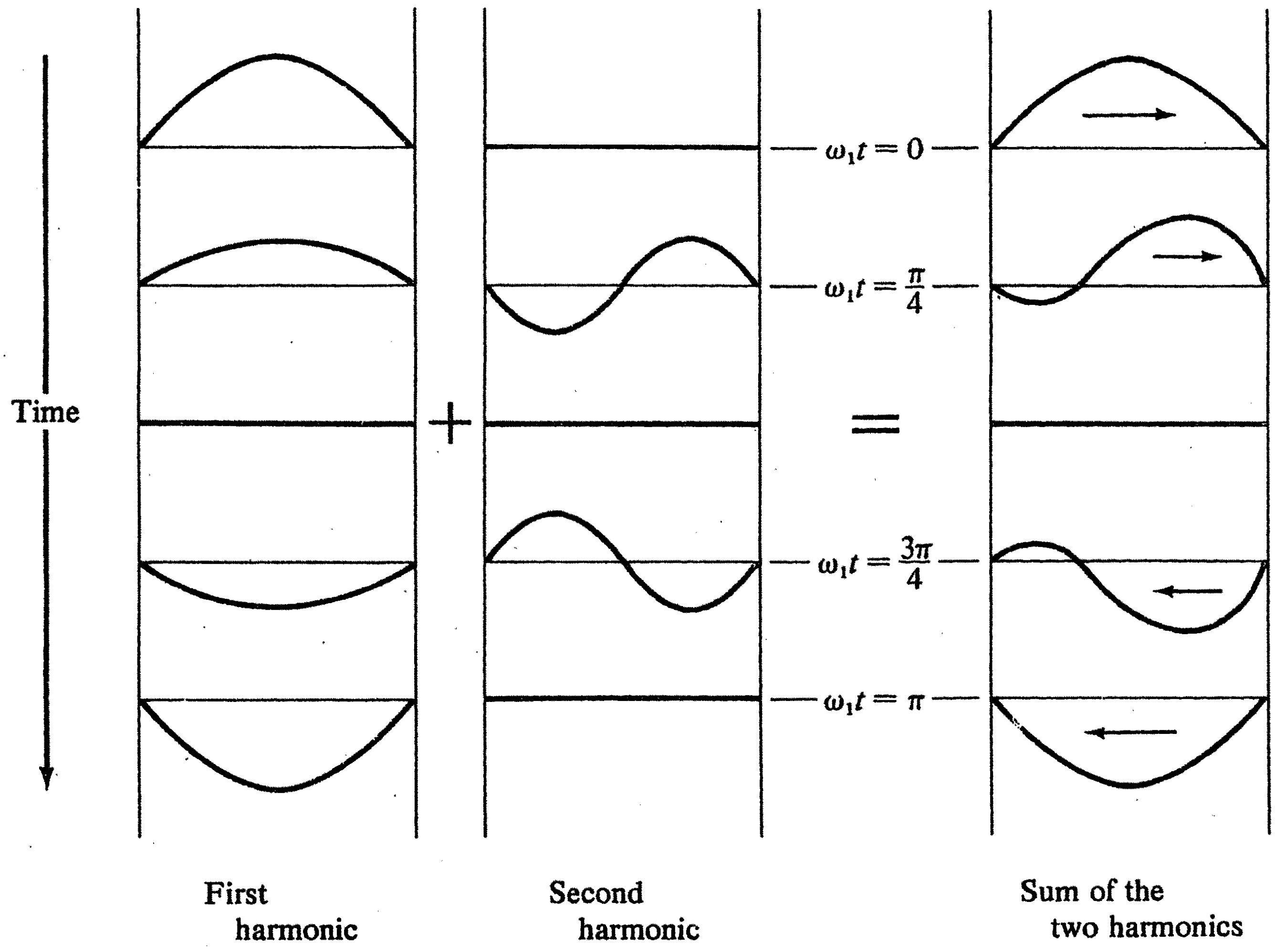
$$u(x,t) = \cos\left(\frac{\pi ut}{l}\right)\sin\left(\frac{\pi x}{l}\right) + \cos\left(\frac{2\pi ut}{l} + \frac{\pi}{2}\right)\sin\left(\frac{2\pi x}{l}\right)$$

Show graphically that the superposition of these standing waves is a traveling wave.

$$u(x,t) = A(t)\sin\left(\frac{\pi x}{l}\right) + B(t)\sin\left(\frac{2\pi x}{l}\right)$$ with $A(t) = \cos(\omega_1 t)$ and $B(t) = \cos\left(2\omega_1 t + \frac{\pi}{2}\right)$

Construct $A(t)$  $+$ $B(t)$ 

$\omega_1 t$	$A(t)=\cos(\omega_1 t)$	$B(t)=\cos\left(2\omega_1 t+\frac{\pi}{2}\right)$
0	1	0
$\pi/4$	$1/\sqrt{2}$	-1
$\pi/2$	0	0
$3\pi/4$	$-1/\sqrt{2}$	1
π	-1	0



The sum of two standing waves is a traveling wave.

3. In PLANCK's theory of blackbody radiation, the density of radiative energy between ν and $\nu + d\nu$ is given by

$$\rho(\nu,T)d\nu = \frac{8\pi h\nu^3}{c^3}\frac{d\nu}{e^{h\nu/k_BT}-1}$$

a. What is the basic non-classical assumption that lead PLANCK to this expression?

$E = nh\nu$ with n nonzero positive integer.

The energy of the electronic atomic oscillators that emit radiation can only take discrete values proportional to the oscillation frequency, i.e. the energy is *quantized*.

b. Show that, for small frequencies, PLANCK's expression reduces to the classical RAYLEIGH-JEANS expression.

$$\rho(\nu,T)d\nu = \frac{8\pi k_BT}{c^3}\nu^2 d\nu$$

Truncating the Taylor series expansion $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + ... + \frac{x^n}{n!} + ...$ to 2nd order with $x = \frac{h\nu}{k_BT}$

$$\rho(\nu,T) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_BT}-1} \sim \frac{8\pi h\nu^3}{c^3}\frac{1}{(1+h\nu/k_BT+\cdots)-1} = \frac{8\pi h\nu^3}{c^3}\frac{k_BT}{h\nu} = \frac{8\pi k_BT}{c^3}\nu^2$$

Can you explain why this is the case in simple terms?

The electronic atomic oscillators that are *active*, i.e. emit radiation, must have a minimum energy $h\nu$ $(n=1)$. For small frequencies, there is enough thermal energy for all the oscillators to have the small required minimum energy $h\nu$ and therefore to be active. Classical physics generally overcounts the number of oscillators, but for small frequencies (or high temperatures) all oscillators are active and quantum expressions reduce to classical ones.

c. Derive the STEFAN-BOLTZMANN law $R = c\,E_{\mathrm{v}}/4 = \sigma T^4$, where R is the radiation energy per unit area and time and E_{v} is the total radiation energy density. Compare your result for the STEFAN-BOLTZMANN constant σ to the experimental value of 5.67 10^{-8} $Jm^{-2}K^{-4}s^{-1}$.

$$R = \frac{cE_V}{4} = \frac{c}{4}\int_0^\infty \rho(\nu,T)d\nu = \frac{c}{4}\frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/k_BT}-1} = \frac{2\pi h}{c^2}\int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/k_BT}-1}$$

Introducing the variable $x = \frac{h\nu}{k_BT}$, one obtains

$$R = \frac{2\pi h}{c^2}\int_0^\infty \left(\frac{k_BT}{h}\right)^4 \frac{x^3dx}{e^x-1} = \frac{2\pi h}{c^2}\left(\frac{k_BT}{h}\right)^4 \int_0^\infty \frac{x^3dx}{e^x-1} = \frac{2\pi h}{c^2}\left(\frac{k_BT}{h}\right)^4 \cdot \frac{\pi^4}{15} = \frac{2\pi^5 k_B^4}{15c^2h^3}\cdot T^4 = \sigma T^4$$

with $\sigma = \frac{2\pi^5 k_B^4}{15c^2h^3} = \frac{2\pi^5(1.38066\cdot 10^{-23}\,JK^{-1})^4}{15\cdot(2.9989\cdot 10^8\,ms^{-1})^2(6.6262\cdot 10^{-34}\,Js)^3} = 5.67\cdot 10^{-8}\,Jm^{-2}K^{-4}s^{-1}$

4. The peak of emission from a hot metal in a steel furnace occurs around 1600 nm. Estimate the temperature of the steel.

Wien displacement law: $\lambda_{\max}T = \frac{hc}{4.965k_B} = \frac{6.6262\cdot 10^{-34}\,Js\cdot 2.9989\cdot 10^8\,ms^{-1}}{4.965\cdot 1.38066\cdot 10^{-23}\,JK^{-1}} = 2.9\cdot 10^{-3}\,mK$

$$T = \frac{2.9\cdot 10^{-3}\,mK}{\lambda_{\max}} = \frac{2.9\cdot 10^{-3}\,mK}{1600\cdot 10^{-9}\,m} = 1812K \sim 1540°C$$

5. The relative positions of the spectral lines observed in the Hydrogen atom emission spectrum can be reproduced by the RYDBERG formula

$$\bar{\nu} = R_H\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \qquad n < m$$

a. According to the Bohr model of the hydrogen atom, the RYDBERG constant can be derived as

$$R_H = \frac{\mu e^4}{8\varepsilon_0^2 h^3 c}$$

What numerical value do you obtain for the RYDBERG constant? How does it compare to the experimental value of 109,678 cm^{-1}.

$$R_H = \frac{\mu e^4}{8\varepsilon_0^2 h^3 c} \qquad \mu = \frac{m_e m_p}{m_e + m_p} = 0.999455\cdot m_e = 9.1046\cdot 10^{-31}\,kg$$

$$R_H = \frac{9.1046\cdot10^{-31}kg\cdot(1.602\cdot10^{-19}C)^4}{8\cdot(8.8542\cdot10^{-12}C^2s^2kg^{-1}m^{-3})^2(6.6262\cdot10^{-34})^3(2.9989\cdot10^{10}cms^{-1})} = 109{,}677cm^{-1}$$

which agrees very well with the experimentally determined value of the Rydberg constant!

b. Calculate the ionization energy of the Hydrogen atom (in eV).

The ionization energy is the energy needed to remove the electron from the H atom, i.e. the gap between the ground state $(n=1)$ and an infinitely excited state $(m=\infty)$ corresponding to the separated electron and proton.

$$\bar{v} = R_H\left(\frac{1}{1^2}-\frac{1}{\infty^2}\right) = R_H = 109{,}678cm^{-1}$$

$$IE = hv = hc\bar{v} = 6.6262\cdot10^{-34}Js\cdot2.9989\cdot10^{10}cms^{-1}\cdot109678cm^{-1} = \frac{2.18\cdot10^{-18}J}{1.602\cdot10^{-19}J/eV} = 13.6eV$$

c. For n=3, calculate the wavelength (in nm) for the first two lines given by the RYDBERG formula. Also calculate the wavelength for the n=3 series limit. What part of the electromagnetic spectrum do these lines belong to?

$$\bar{v} = R_H\left(\frac{1}{3^2}-\frac{1}{4^2}\right) = 5331\ cm^{-1} \qquad \lambda = \frac{1}{\bar{v}} = 1.876\cdot10^{-4}cm = 1.876\cdot10^{-6}m = 1876nm$$

$$\bar{v} = R_H\left(\frac{1}{3^2}-\frac{1}{5^2}\right) = 7799\ cm^{-1} \qquad \lambda = \frac{1}{\bar{v}} = 1.282\cdot10^{-4}cm = 1.282\cdot10^{-6}m = 1282nm$$

series limit: $\bar{v} = R_H\left(\frac{1}{3^2}\right) = 12186\ cm^{-1}$ $\qquad \lambda = \frac{1}{\bar{v}} = 0.820\cdot10^{-4}cm = 0.820\cdot10^{-6}m = 820nm$

These lines belong to the near-IR region of the electromagnetic spectrum (IR close to visible) and this series is called the Paschen series.

6. a. Calculate the radius of the first electronic orbit in the BOHR model of the Hydrogen atom. Calculate the velocity of an electron in the first orbit.

H atom: $Z=1$ First orbit (ground state): $n=1$

$$r = \frac{\varepsilon_0 h^2 n^2}{\pi \mu Z e^2} = \frac{(8.8542 \cdot 10^{-12} C^2 s^2 kg^{-1} m^{-3}) \cdot (6.6262 \cdot 10^{-34} Js)^2 \cdot 1}{\pi \cdot (9.1046 \cdot 10^{-31} kg) \cdot 1 \cdot (1.602 \cdot 10^{-19} C)^2} = 5.29 \cdot 10^{-11} m = 0.529 \mathring{A}$$

$$v = \sqrt{e^2 / 4\pi\varepsilon_0 \mu r}$$

or $$v = \frac{n\hbar}{\mu r} = \frac{1 \cdot 6.6262 \cdot 10^{-34} Js}{2\pi \cdot 9.1046 \cdot 10^{-31} kg \cdot 5.29 \cdot 10^{-11} m} = 2.19 \cdot 10^6 ms^{-1}$$ ~1% the speed of light!

b. Calculate the wavelength associated with that electron. What can you conclude of the wave nature of the electron in the Hydrogen atom?

DeBroglie postulate $$\lambda = \frac{h}{p} = \frac{h}{\mu v} = \frac{6.6262 \cdot 10^{-34} Js}{9.1046 \cdot 10^{-31} kg \cdot 2.19 \cdot 10^6 ms^{-1}} = 3.32 \cdot 10^{-10} m = 3.32 \mathring{A}$$

The electron wavelength is of similar magnitude as the physical dimension of the atom (radius of first orbit ~ 0.5Å), so the wave nature of an electron typically traveling at 1% the speed of light in an atom is significant. As a matter of fact, the wave nature of electrons was proved by interference and diffraction experiments. The wave-particle duality applies to microscopic objects such as electrons, but not to macroscopic objects. The wavelength of electrons (~Å) at typical velocities in atoms lies in the X-ray region of the electromagnetic spectrum, therefore X-rays will excite electrons in atoms; conversely, accelerating electrons in atoms will emit X-rays.

c. What is the uncertainty in the momentum of an electron that we wish to locate within 50 pm? What can you conclude?

$$\Delta x = 50 \cdot 10^{-12} m = 0.5 \mathring{A}$$

Using Heisenberg uncertainty principle $$\Delta p \approx \frac{h}{\Delta x} = \frac{6.6262 \cdot 10^{-34} Js}{50 \cdot 10^{-12} m} = 1.3 \cdot 10^{-23} kg \cdot ms^{-1}$$

This translates into an uncertainty in the velocity $$\Delta v = \frac{\Delta p}{m_e} = \frac{1.3 \cdot 10^{-23} kg \cdot ms^{-1}}{9.10953 \cdot 10^{-31} kg} = 1.45 \cdot 10^7 ms^{-1}$$

which is of the same order of magnitude as (it is actually larger than) the velocity of an electron in an atom itself (recall $v = 2.19 \cdot 10^6 ms^{-1}$). The Bohr model of the H atom violates the Heisenberg uncertainty principle, as it infers exact knowledge of the position and momentum of the electron in the H atom. As this calculation shows, if we wish to locate the electron in an atom with reasonable accuracy ($\Delta x = 0.5 \mathring{A}$, which is consistent with the physical dimension of the atom), then we end up with huge uncertainty in the electron velocity. The Heisenberg uncertainty principle applies to microscopic objects traveling at high velocities such as electrons in atoms, but not to macroscopic objects.

7. a. What is the work function of a metal?

The work function of a metal is defined as the minimum energy required to extract an electron from the metal surface. It is the bulk analog of ionization energies for atoms and molecules and represents the binding energy of the electron to a metal.

b. The work function of Nickel is 5 eV. Calculate the kinetic energy (in eV) of the electrons ejected from the metal following radiation by light of wavelength 500 and 100 nm?

$$\phi = 5eV = 5eV \cdot \frac{1.602 \cdot 10^{-19} J}{1eV} = 8.01 \cdot 10^{-19} J \qquad \frac{1}{2} m\mathrm{v}^2 + \phi = hv$$

$$\lambda = 500nm \qquad hv = \frac{hc}{\lambda} = \frac{6.6262 \cdot 10^{-34} Js \cdot 2.9989 \cdot 10^{8} ms^{-1}}{500 \cdot 10^{-9} m} = 3.98 \cdot 10^{-19} J = 2.48eV$$

The incident photon does not have enough energy to extract an electron from the Nickel surface. No photoelectric effect will be observed.

$$\lambda = 100nm \qquad hv = \frac{hc}{\lambda} = \frac{6.6262 \cdot 10^{-34} Js \cdot 2.9989 \cdot 10^{8} ms^{-1}}{100 \cdot 10^{-9} m} = 1.99 \cdot 10^{-18} J = 12.4eV$$

$$\frac{1}{2} m\mathrm{v}^2 = hv - \phi = 12.4eV - 5eV = 7.4eV$$

The kinetic energy of the ejected electrons is 7.4eV.

c. What is the name of this physical phenomenon?

Ejection of electrons from a metal plate upon irradiation is called the photoelectric effect, first discovered by Hertz in the late 1880s.

d. Who obtained the Nobel Prize in Physics in 1921 for providing an explanation to this phenomenon (in 1905)?

Albert Einstein

Constants

$$\hbar = \frac{h}{2\pi}$$

h = 6.62618 10^{-34} J.s

c = 2.997925 10^{8} m.s^{-1}

e = 1.602 10^{-19} C

ε_0 = 8.8542 10^{-12} C^2.s^2.kg^{-1}.m^{-3}

k_B = 1.38066 10^{-23} J.K^{-1}

N_A = 6.02 10^{23}

m_e = 9.10953 10^{-31} kg

m_p = 1.67265 10^{-27} kg

m_O = 16.0 g/mol

Units

$1\,eV$ = 1.602 10^{-19} J

1 Å = 10^{-10} m

Elements of Mathematics

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + ... + \frac{x^n}{n!} + ...$$

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

Equations

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$V = \frac{1}{2} k x^2 \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\nu = \frac{c}{\lambda} \qquad \bar{\nu} = \frac{1}{\lambda} \qquad \lambda = \frac{h}{p}$$

$$\lambda_{\max} T = \frac{hc}{4.965 k_B}$$

$$\frac{1}{2} m\text{v}^2 + \phi = h\nu \qquad p = m\text{v}$$

$$r = \frac{\varepsilon_0 h^2 n^2}{\pi \mu Z e^2} \qquad \text{v} = \sqrt{e^2 / 4\pi\varepsilon_0 \mu \text{r}}$$

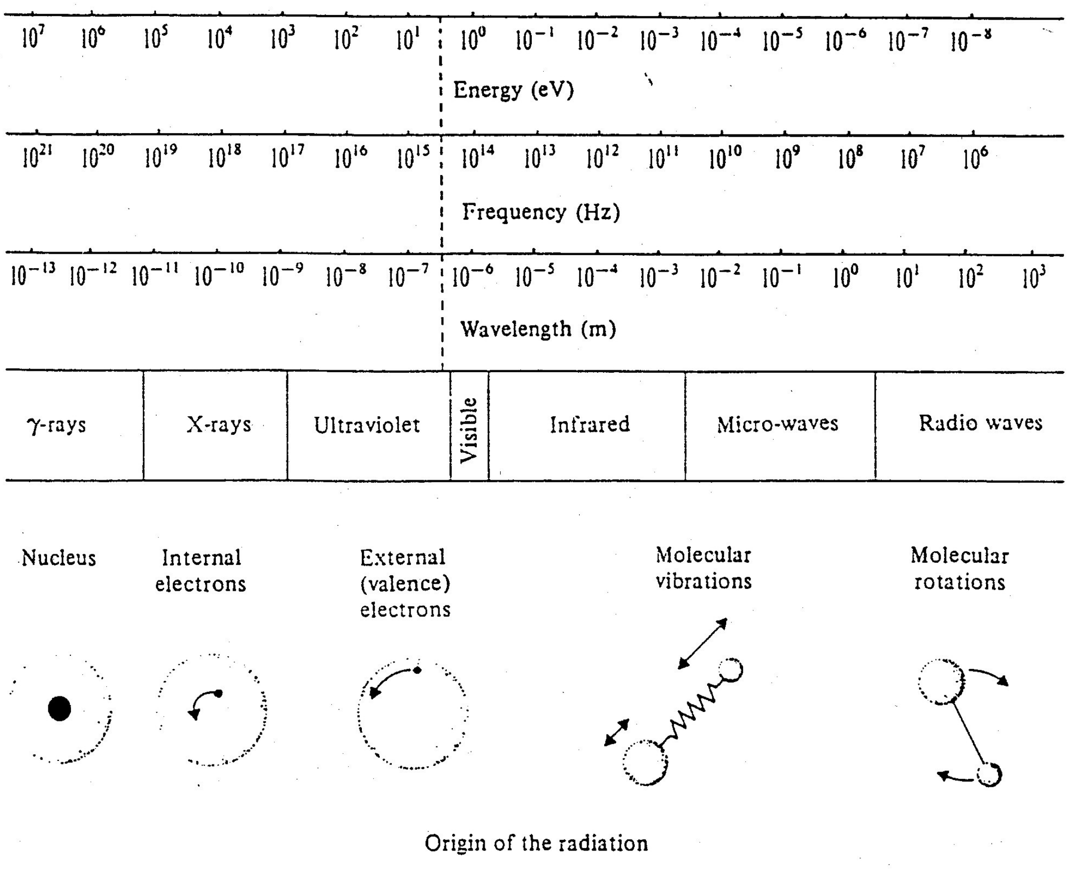
$$\ell = \mu \text{v} r = n\hbar$$

$$\Delta x \cdot \Delta p \approx h$$

Figure: the electromagnetic spectrum

Adapted from *Quantics, Rudiments of Quantum Physics*, Lévy-Leblond and Balibar, Elsevier, 1989.

Corresponding to each region of the spectrum, its usual origin – molecular, atomic or nuclear – has been indicated (the shaded 'balls' schematize the atoms).



Visible: typically 300-900 nm