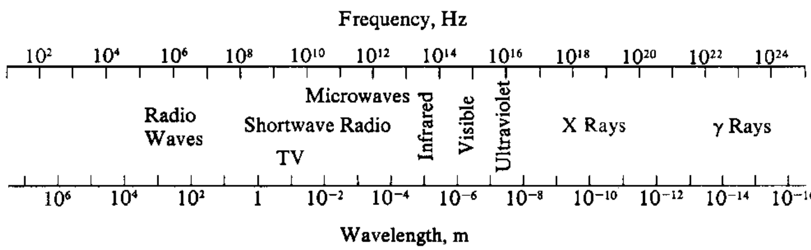
Quantum Chemistry
Corrections 1

1. Radiation in the ultraviolet region of the electromagnetic spectrum is usually described in terms of wavelength, λ, and is given in units of angstrom (1 Å = 10^{-10} m) or nanometers (10^{-9} m). Calculate ν, $\tilde{\nu}$, and the energy, E, for ultraviolet radiation with λ=2000 Å and compare your results to the figure below.



$$\nu = \frac{c}{\lambda} = \frac{3 \cdot 10^{8}\left[\mathrm{m \cdot s^{-1}}\right]}{2000 \cdot 10^{-10}\left[\mathrm{m}\right]} = 1.5 \cdot 10^{15}\ \mathrm{Hz}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{2000 \cdot 10^{-10}\left[\mathrm{m}\right]} = 5 \cdot 10^{6}\left[\mathrm{m^{-1}}\right] = 5 \cdot 10^{4}\ \mathrm{cm^{-1}}$$

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \cdot 10^{-34}\left[\mathrm{J \cdot s}\right] \cdot 3 \cdot 10^{8}\left[\mathrm{m \cdot s^{-1}}\right]}{2000 \cdot 10^{-10}\left[\mathrm{m}\right]} = 9.94 \cdot 10^{-19}\ \mathrm{J}$$

2. Given that the work function of chromium is 4.4 eV,

- ***Calculate the maximum wavelength of light able to remove electron from a chromium surface.***

$$h\frac{c}{\lambda} = K + \phi_{0}$$

the wavelength is at maximum when the kinetic energy has its minimum (K=0)

$$h\frac{c}{\lambda_{max}} = \phi_{0}$$

$$\lambda_{max} = \frac{hc}{\phi_{0}} = \frac{6.626 \cdot 10^{-34}\, Js \cdot 3 \cdot 10^{8}\,\frac{m}{s}}{(4.4eJ \cdot \frac{1.6 \cdot 10^{-19}\, J}{1eV})} = 2.82 \cdot 10^{-7}\, m = 282nm$$

- ***Calculate the kinetic energy of electrons emitted from a chromium surface when it is irradiated with ultraviolet radiation of wavelength 2000 Å***

$$K = h\nu - \phi_{0} = h\frac{c}{\lambda} - \phi_{0} = \frac{6.626 \cdot 10^{-34}\, Js \cdot 3 \cdot 10^{8}\,\frac{m}{s}}{2000 \cdot 10^{-10}\, m} - (4.4eV \cdot \frac{1.6 \cdot 10^{-19}\, J}{1eV}) = 2.90 \cdot 10^{-19}\, J$$

$$K_{eV} = 2.90 \cdot 10^{-19} J \cdot \frac{1eV}{1.6 \cdot 10^{-19} J} = 1.81 eV$$

- ***What is the stopping potential for these electrons?***

$$V_s = \frac{K}{e} = 1.8 \text{ V}$$ (this is why it is important to express the stopping potential in eV).

3. ***A homogeneous light beam of wavelength λ=300 nm and intensity $5 \cdot 10^{-2}$ W m^{-2} falls on a sodium surface. The photoelectric work function for sodium is 2.3 eV. Calculate:***
   - ***the average number of photon striking the surface per m^2 and per second***
   - ***the average number of electrons emitted per m^2 and per second***
   - ***the maximum kinetic energy of the photoelectrons***

A photon of λ=300 nm has an energy of:

$$E = \frac{hc}{\lambda} = 6.63.10^{-19} [\text{J}] = 4.14 \text{ eV}$$

- The intensity of the light is equal to the energy of the *N* photons per unit time, per unit area:

$$I = Nh\nu = 5.10^{2} \text{ Js}^{-1}\text{m}^{-2}$$

Therefore, the number of photons colliding with the surface per m^2 and per second is then:

$$N = \frac{I}{h\nu} = 7.55.10^{16} \text{ photons s}^{-1}\text{m}^{-2}$$

- If we consider the ideal case in which one photon always ejects one electron, the number of electrons emitted per m^2 and second is:

$$N_e = N_\gamma = 7.55.10^{16} \text{ electrons s}^{-1}\text{m}^{-2}$$

- The maximum kinetic energy of the emitted photoelectrons is:

$$K = h\nu - \phi = 1.84 \ eV$$

4. ***According to Planck's law the energy per unit time radiated per unit area per unit frequency by a black body at a temperature T is given by:***

$$I(\lambda, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

a. ***From this derive Wien's displacement law which relates the wavelength at which the intensity per unit wavelength of the radiation produced by a black body is at a maximum to the temperature of the black body.***

When we want to pass from the previous formula to a new one that is expressed in function of the wavelength, we cannot just replace the frequency for the wavelength, since we have to take into account that an increment in frequency determines a decrement in wavelength.

In other words: the intensity of the radiation emitted within the frequency interval $d\nu$, that includes the frequency ν, is equal to the intensity of radiation emitted within each $d\lambda$ interval with central wavelength λ.

$$I(\lambda,T)d\lambda = I(\nu,T)d\nu$$

and at this point we effectively obtain the expression of the intensity of radiation in function of λ, for every value of λ.

$$I(\lambda,T) = -\frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda kT}}-1}$$

if we want to find the maximum, we will derive the previous expression for the wavelength and solve the following equation:

$$\frac{\partial I(\lambda,T)}{\partial \lambda} = 0$$

$$\frac{\partial I(\lambda,T)}{\partial \lambda} = 2hc^2\left[\frac{-\left(5\lambda^4(e^{\frac{hc}{\lambda kT}}-1)+\lambda^5(-\frac{hc}{\lambda^2 kT})e^{\frac{hc}{\lambda kT}}\right)}{\lambda^{10}(e^{\frac{hc}{\lambda kT}}-1)^2}\right] =$$

$$= 2hc^2\left[\frac{hc}{\lambda^7 kT}\frac{e^{\frac{hc}{\lambda kT}}}{(e^{\frac{hc}{\lambda kT}}-1)^2} - \frac{5}{\lambda^6(e^{\frac{hc}{\lambda kT}}-1)}\right] =$$

$$= 2hc^2\left[\frac{hc}{\lambda^7 kT}\frac{e^{\frac{hc}{\lambda kT}}}{(e^{\frac{hc}{\lambda kT}}-1)^2} - \frac{5\lambda(e^{\frac{hc}{\lambda kT}}-1)}{\lambda^7(e^{\frac{hc}{\lambda kT}}-1)^2}\right] =$$

$$= \frac{2hc^2}{\lambda^7}\frac{1}{(e^{\frac{hc}{\lambda kT}}-1)^2}\left[\frac{hc}{kT}e^{\frac{hc}{\lambda kT}} - 5\lambda(e^{\frac{hc}{\lambda kT}}-1)\right] = 0$$

that means:

$$\left[\frac{hc}{kT}e^{\frac{hc}{\lambda kT}} - 5\lambda(e^{\frac{hc}{\lambda kT}}-1)\right] = 0$$

if we call:

$$x = \frac{hc}{\lambda kT}$$

we end up with:

$$[xe^x - 5(e^x - 1)] = 0$$

and by knowing the numerical solution for the previous equation:

$$x = 4.965$$

$$x = \frac{hc}{\lambda kT} = 4.965$$

We can solve for $\lambda_{\max}$:

$$\lambda_{\max} = \frac{hc}{4.965 \cdot kT} = \frac{6.626 \cdot 10^{-34}\, Js \cdot 3 \cdot 10^{8}\, \frac{m}{s}}{1.38 \cdot 10^{-23}\, \frac{J}{K} \cdot 4.965 \cdot T}$$

$$\lambda_{\max} = \frac{0.002901 m \cdot K}{T}$$

b. Assuming that the sun can be described as a black body and knowing that the wavelength of maximum emission intensity is 500 nm, calculate the temperature of the sun.

From the equation found above:

$$\lambda_{\max} = \frac{0.002901 m \cdot K}{T} = 500 \cdot 10^{-9}\, m$$

$$T = 5802K$$

5. Show that the Lyman series occurs between 912 Å and 1216 Å, that the Balmer series occurs between 3630 Å and 6563 Å, and that the Paschen series occurs between 8210 Å and 18760 Å. Identify the spectral regions to which these wavelengths correspond.

$$\tilde{\nu}_{n_1 \leftarrow n_2} = R_H \left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}} \right) \quad \text{with} \quad R_H = \frac{\mu_e e^4}{8 \varepsilon_0^{\,2} c h^3} = 109677\ \text{cm}^{-1}$$

The limits of each of the series correspond with transitions from the highest (n= ∞) and from the lowest possible energy level.

Lyman: (UV)

$$\begin{cases} \tilde{\nu}_{1\leftarrow\infty} = R_H \lim\limits_{n\to\infty} \left(\frac{1}{1^2} - \frac{1}{n^2} \right) = R_H = 109677 \left[\text{cm}^{-1} \right] \Rightarrow \lambda_{1\leftarrow\infty} = 912\ \text{Å} \\ \tilde{\nu}_{1\leftarrow 2} = R_H \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} R_H = 82258 \left[\text{cm}^{-1} \right] \Rightarrow \lambda_{1\leftarrow 2} = 1216\ \text{Å} \end{cases}$$

Balmer: (visible)

$$\begin{cases} \tilde{\nu}_{2\leftarrow\infty} = R_H \lim\limits_{n\to\infty} \left(\frac{1}{2^2} - \frac{1}{n^2} \right) = \frac{1}{4} R_H = 27419 \left[\text{cm}^{-1} \right] \Rightarrow \lambda_{2\leftarrow\infty} = 3647\ \text{Å} \\ \tilde{\nu}_{2\leftarrow 3} = R_H \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{36} R_H = 15233 \left[\text{cm}^{-1} \right] \Rightarrow \lambda_{2\leftarrow 3} = 6565\ \text{Å} \end{cases}$$

Paschen:

$$\begin{cases} \tilde{\nu}_{3\leftarrow\infty} = R_H \lim_{n\to\infty}\left(\frac{1}{3^2}-\frac{1}{n^2}\right) = \frac{1}{9}R_H = 12186\left[\text{cm}^{-1}\right] \Rightarrow \lambda_{3\leftarrow\infty} = 8206\ \text{Å} \\ \tilde{\nu}_{3\leftarrow 4} = R_H\left(\frac{1}{3^2}-\frac{1}{4^2}\right) = \frac{7}{144}R_H = 5332\left[\text{cm}^{-1}\right] \Rightarrow \lambda_{3\leftarrow 4} = 18760\ \text{Å} \end{cases} \quad \text{(IR)}$$

6. Calculate the de Broglie wavelength for:

- ***an electron with a kinetic energy of 100 eV***
- ***a proton with a kinetic energy of 10^5 eV***

$$\left.\begin{array}{l} \lambda = \frac{h}{p} = \frac{h}{mv} \\ mv = \sqrt{m^2v^2} = \sqrt{2mK} \end{array}\right\} \Rightarrow \lambda = \frac{h}{\sqrt{2mK}}$$

- **an electron with a kinetic energy of 100 eV**

$$\left.\begin{array}{l} m_e = 9.11\cdot 10^{-31}\left[\text{kg}\right] \\ K_e = 100\left[\text{eV}\right] = 1.6\cdot 10^{-17}\left[\text{J}\right] \end{array}\right\} \Rightarrow \lambda_e = \frac{6.626\cdot 10^{-34}\left[\text{J}\cdot\text{s}\right]}{\sqrt{2\cdot 9.11\cdot 10^{-31}\left[\text{kg}\right]\cdot 1.6\cdot 10^{-17}\left[\text{J}\right]}} = 1.23\ \text{Å}$$

N.B.: $\text{v}_e = \sqrt{\frac{2K_e}{m_e}} = 5.93\cdot 10^6\left[\text{m}\cdot\text{s}^{-1}\right] \cong 0.02c \Rightarrow$ we neglect relativistic effects

- **a proton with a kinetic energy of 10^5 eV**

$$\left.\begin{array}{l} m_p = 1.67\cdot 10^{-27}\left[\text{kg}\right] \\ K_p = 10^5\left[\text{eV}\right] = 1.6\cdot 10^{-14}\left[\text{J}\right] \end{array}\right\} \Rightarrow \lambda_p = \frac{6.626\cdot 10^{-34}\left[\text{J}\cdot\text{s}\right]}{\sqrt{2\cdot 1.67\cdot 10^{-27}\left[\text{kg}\right]\cdot 1.6\cdot 10^{-14}\left[J\right]}} = 9.06\cdot 10^{-4}\ \text{Å}$$

N.B.: $\text{v}_p = \sqrt{\frac{2K_p}{m_p}} = 4.38\cdot 10^6\left[m\cdot s^{-1}\right] \cong 0.015c \Rightarrow$ we neglect relativistic effects