CHEMISTRY Test n°1 16/10/2019 – Some answers and comments

	Problem 1 : Preliminary question	**Some comments**
	E(J) = $\frac{\mathrm{hc}}{\lambda}$ with h in J.s, c in m/s and λ in m. To express in eV, and having λ(Å) = λ(m)*10^{10} E(eV) = $\frac{\mathrm{E(J)}}{\mathrm{e}} = \frac{\mathrm{hc}}{\lambda.10^{-10}.\mathrm{e}} = \frac{12400}{\lambda\,(\mathrm{A°})}$ with h in J.s, c in m/s and λ in Å. n : integer values ≥ 1 or 1, 2, 3, 4…n l : integers values 0 ≤l ≤ n-1 or 0, 1, 2, 3, 4…(n-1) m :integer values -l ≤ m ≤ +l or -l, -l+1…. 0…., l-1, l s : ± 1/2	The relation $E = \frac{hc}{\lambda}$ is not de Broglie's equation as found in some copies! (no penalty)
	Problem 2 : Indentification of a hydrogen-like system	**Some comments**
b)	In the absorption spectrum, the transition with greater energy corresponds to ionization : transition level : 1→∞ Ritz Balmer applied to hydrogen-like systems: $\frac{1}{\lambda} = R_X Z^2 \left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$ thus here : n = 1 and n'→ ∞ $\frac{1}{\lambda_{1\to\infty}} = R_X Z^2$ $Z = \sqrt{\frac{1}{R_X \lambda_{1\to\infty}}} = \sqrt{\frac{1}{109677{,}8 * 25{,}3310^{-8}}} = 6$ With R_X~R_H (cm^{-1}) and λ (cm) $E = \frac{hc}{\lambda}$ or from E(eV) = $\frac{12400}{\lambda\,(\mathrm{A°})}$ result of question 1 : E_i = 489,54 eV = 489,5 eV	In the Bohr model, the transition is from a level (not a *subshell*, not an *orbital*) and involves the unique electron (not *an* electron) By the way, the relation $E = \frac{hc}{\lambda}$ is not de Broglie's equation as it found in some copies! (no penalty) Literal expressions were often given, but some mathematical errors were found. Indeed, if λ is used in (m) then R_X should be expressed in (m^{-1}); if you keep R_X in (cm^{-1}), then λ should be expressed in (cm).

<table>
<tr><th colspan="2">Problem 3 : Study of Beryllium</th><th>Some comments</th></tr>
<tr><td></td><td>Electronic configuration of Be $1s^2$ $2s^2$

$1s^2$: (n = 1, l = 0, m_l = 0; s = + ½) and (n = 1, l = 0, m_l = 0; s = - ½)

$2s^2$: (n = 2, l = 0, m_l = 0; s = + ½) and (n = 2, l = 0, m_l = 0; s = - ½)</td><td>For this; you should apply the Building up principle and know how to compute and the meaning of each quantum number:

n : integer values ≥ 1 or 1, 2, 3, 4…n
l : integers values 0 ≤l ≤ n-1 or 0, 1, 2, 3, 4…(n-1)
m :integer values -l ≤ m ≤ +l or -l, -l+1…. 0…., l-1, l
s : ± 1/2</td></tr>
<tr><td>b)</td><td>Hydrogen-like ion (HLI) derived from Be contains only 1 electron: Be^{3+} $1s^1$

According to Ritz-Balmer equation generalized to HLI

$\Delta \mathrm{E}_{n\to\infty} = \frac{\mathrm{hc}}{\lambda_{n\to\infty}} = \mathrm{hcR_X Z^2}\left(\frac{1}{\mathrm{n}^2} - 0\right) = \lvert E_n - E_\infty \rvert = 0 - En = -En$ as En<0

And E∞ = 0

ifi n =1 E_1= $-\mathrm{hcR_X Z^2}$.

For any value of n : thus $\mathrm{E}_n = -\frac{\mathrm{hcR_X Z^2}}{\mathrm{n}^2} = \frac{E1}{\mathrm{n}^2}$

E_1 = - 217.60 eV

E_2 = - 54.40 eV

E_3 = - 24.18 eV

E_4 = -13.60 eV</td><td></td></tr>
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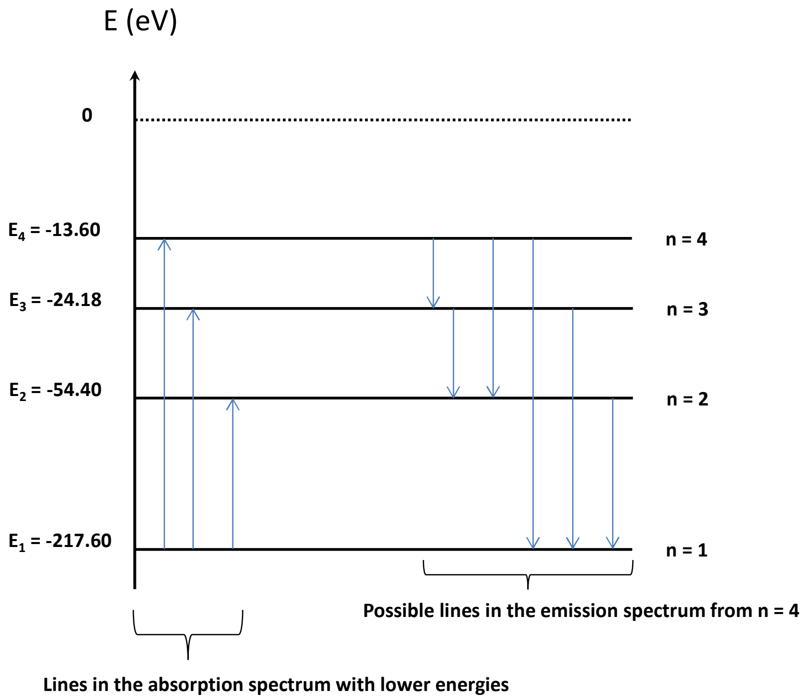
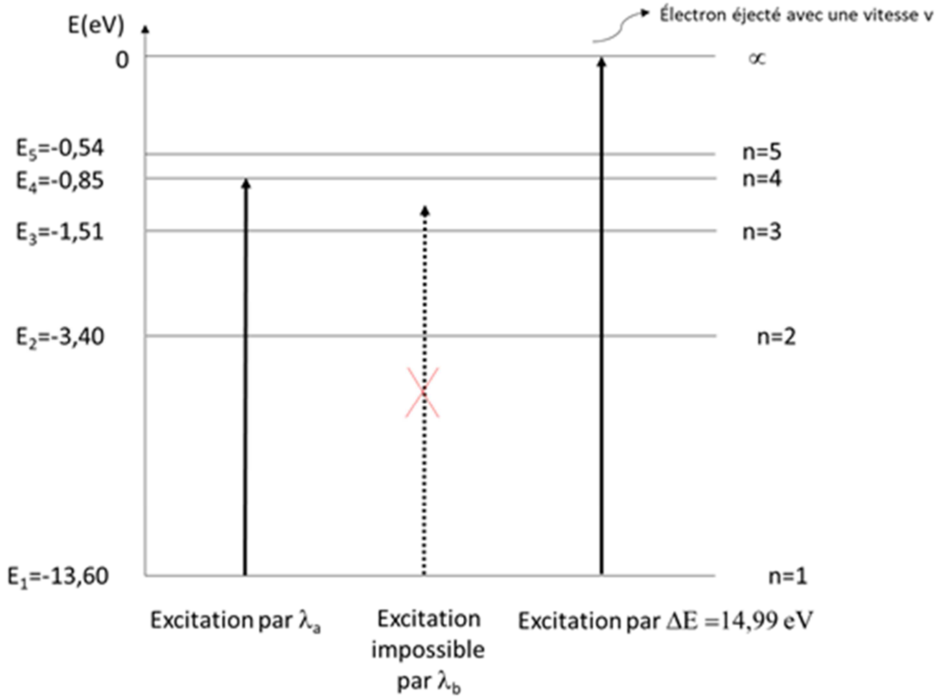
		This diagram requires : - A legend (E(eV)) - The origin of the energy scale for n $\rightarrow\infty$ Each energy level (up to n = 4), with the associated energy (value or identification E_1…)
d)	Two extrema values in the absorption spectrum : **Short-wavelength limit** (highest possible energy): $\boldsymbol{\lambda_{1\to\infty}} = \frac{1}{R_X Z^2} = \frac{12400}{E_\infty - E_1}$ = 56.99 Å = 57.0 Å **Long-wavelength limit** (lowest possible energy) : $\boldsymbol{\lambda_{1\to 2}} = \frac{1}{R_X Z^2} \times \frac{4}{3} = \frac{12400}{E_2 - E_1} =$ 75.98 Å = 76.0 Å	Absorption spectrum gathers transition lines starting necessarily from **n = 1**
e)	3 absorption rays of lower energies : $\boldsymbol{\lambda_{1\to 2}} = \frac{12400}{E_2 - E_1} =$ 75,98 Å = **76.0 Å**	**Absorption spectrum** (see previous remark)

	$\lambda_{1\text{-}3} = \frac{12400}{E_3 - E_1}$= 64,11 Å = **64.1 Å** $\lambda_{1\text{-}4} = \frac{12400}{E_4 - E_1} = 60{,}78\ \text{Å} = \mathbf{60.8}\ \text{Å}$	
f)	Ionization energy is by definition: $E_i = \lvert E_1 - E_\infty \rvert = 0 - E_1 = -E_1$ = 217.6 eV	
g)	Drawing of 6 emission lines if starting from n = 4 $$E_{n'} - E_n = \frac{12400}{\lambda_{n' \to n}}$$ $\lambda_{4\to1}$ = 60.8 Å ; $\lambda_{3\to1}$ = 64.1 Å ; $\lambda_{2\to1}$ = 76.0 Å $\lambda_{4\to2}$ = 303.9 Å ; $\lambda_{4\to3}$ = 1172.0 Å ; $\lambda_{3\to2}$ = 410.3 Å	If we consider the emission lines that may appear if one starts from n = 4, then remember that emission with intermediate steps may also happen: thus if the first line is from (4 to 3), then we may have other transitions such as (3 to 2) and (2 to 1) or (3 to 1). Etc… Thus, there is a total of 6 possible lines if starting from n = 4.
h)	All lines belong to the UV domain	

	Problem 4 : Hydrogen spectroscopy	Some Comments
	We deal first with a hydrogen atom in its fundamental state. From Ritz Balmer equation (see previous relationship, we can settle that : $$E_n = -\frac{hcR_H}{n^2} = \frac{E_1}{n^2}$$ With E_1 = -13.60 eV E_2 = -3.40 eV E_3 = -1.51 eV E_4 = -0.85 eV E_5 = -0.54 eV…	
	Method a): According to Ritz-Balmer, we have for absorption : $\Delta E_{1\to n} = \frac{hc}{\lambda_{excitation}} = hcR_H\left(1 - \frac{1}{n^2}\right)$ thus $n = \sqrt{\frac{1}{1-\frac{1}{\lambda_{excitation}R_H}}}$ For a given $\lambda_{excitation}$; if we get for n: - An integer value, then we get the arrival level and the phenomenon is absorption - A fraction, then there is no absorption phenomenon as the excitation energy has to match exactly the energy difference between two levels.	
	Method b): An absorption corresponds to the transition from n = 1 to an upper level, with the energy of the incoming radiation being : $$\Delta E_{1\to n}(eV) = \frac{12400}{\lambda_{excitation}(\text{Å})} = \lvert E_n - E_1\rvert = E_n - E_1$$	

	$E_n = \dfrac{12400}{\lambda_{excitation}\,(\mathrm{\AA})} + E_1$ Considering the value of $\lambda_{excitation}$ and E_1 for H, if E_n corresponds to one of the energy of a level for H, then there is an absorption.	
	<u>Situation 1 :</u> $\lambda_{excitation}$ = 97.25 nm From method a) $n = \sqrt{\frac{1}{1-\frac{1}{\lambda_{excitation} R_H}}}$ = **4** **There is thus absorption from n = 1 to n = 4** From method b) E_{ex}=12400/972.5=12.75 eV = $\lvert E_{arrival} - E_1 \rvert$ such that $E_{arrival}$ = - 0.85 eV that is the energy of level 4. **There is thus absorption from n = 1 to n = 4**.	Some confusion here : - Many of you have used the value of the *incoming radiation* and concluded that it does not belong to the visible range: the reasoning is WRONG. The value of the wavelength given in the subject is the one of the incoming radiation (that lead to excitation or not) and not the one of the emitted photon. By the way, there was some confusion on the transition during absorption: when describing the transition, it involves the transition from n = 1 to n = 4 , and not from n = 4 to n = 1!!!
	<u>Situation 2 :</u> $\lambda_{excitation}$ = 101.39 nm From method a) $n = \sqrt{\frac{1}{1-\frac{1}{\lambda_{excitation} R_H}}}$ = **3.15** **There is thus no absorption as the arrival level is not an integer value** From method b) E_{ex}=12400/10139 =12.23 eV = $\lvert E_{arrival} - E_1 \rvert$ such that $E_{arrival}$ = - 1.37 eV that does not correspond to any possible arrival level. **There is thus no absorption**	

c)	<u>Situation 3 :</u> The energy provided is larger than the ionization energy that is $\|E_\infty - E_1\|$ = 13.60 eV. There is thus ionization, end the ejected electron owns as kinetic energy the difference between the incoming energy and the ionization energy: $E_{kinetic} = \|E_{excitation} - E_{ionization}\| = ½ mv^2$ $E_{kinetic}$ = 1.39 eV thus $E_{kinetic}$ = (1.39*e) in J = $1/2mv^2$ Thus the speed of the electron is $v = \sqrt{\frac{2eE_{kinetic}}{m}} = \sqrt{\frac{2*1.602.10^{-19}*1.39}{9.109.10^{-31}}}$ = **701600 m.s^{-1}** = 701.6 km.s^{-1}	

Électron éjecté avec une vitesse v
E(eV)
0
∝
E5=-0,54
n=5
E4=-0,85
n=4
E3=-1,51
n=3
E2=-3,40
n=2
E1=-13,60
n=1
Excitation par λa
Excitation impossible par λb
Excitation par ΔE =14,99 eV