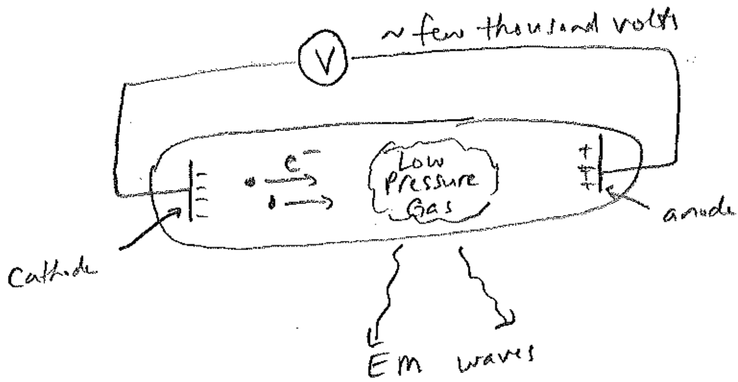
Discrete spectra

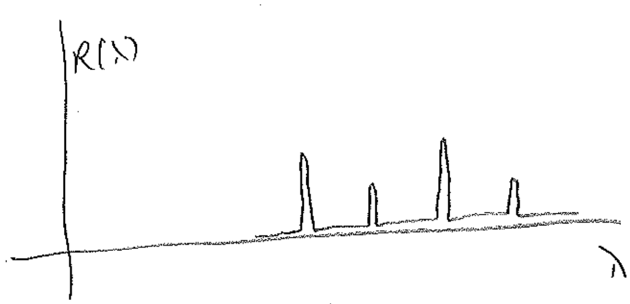
Hot solids, liquids, high pressure gases
emit continuous thermal spectra, but
excited low pressure gases emit discrete spectra.

[How excite gases? Bombard them with electrons]

Gas discharge tube (CRT) [we saw this earlier, w/ bremsstrahlung]



electrons transfer (kinetic) energy to gas atoms, exciting them to higher energy states. Gas atoms then emit EM radiation at discrete wavelengths



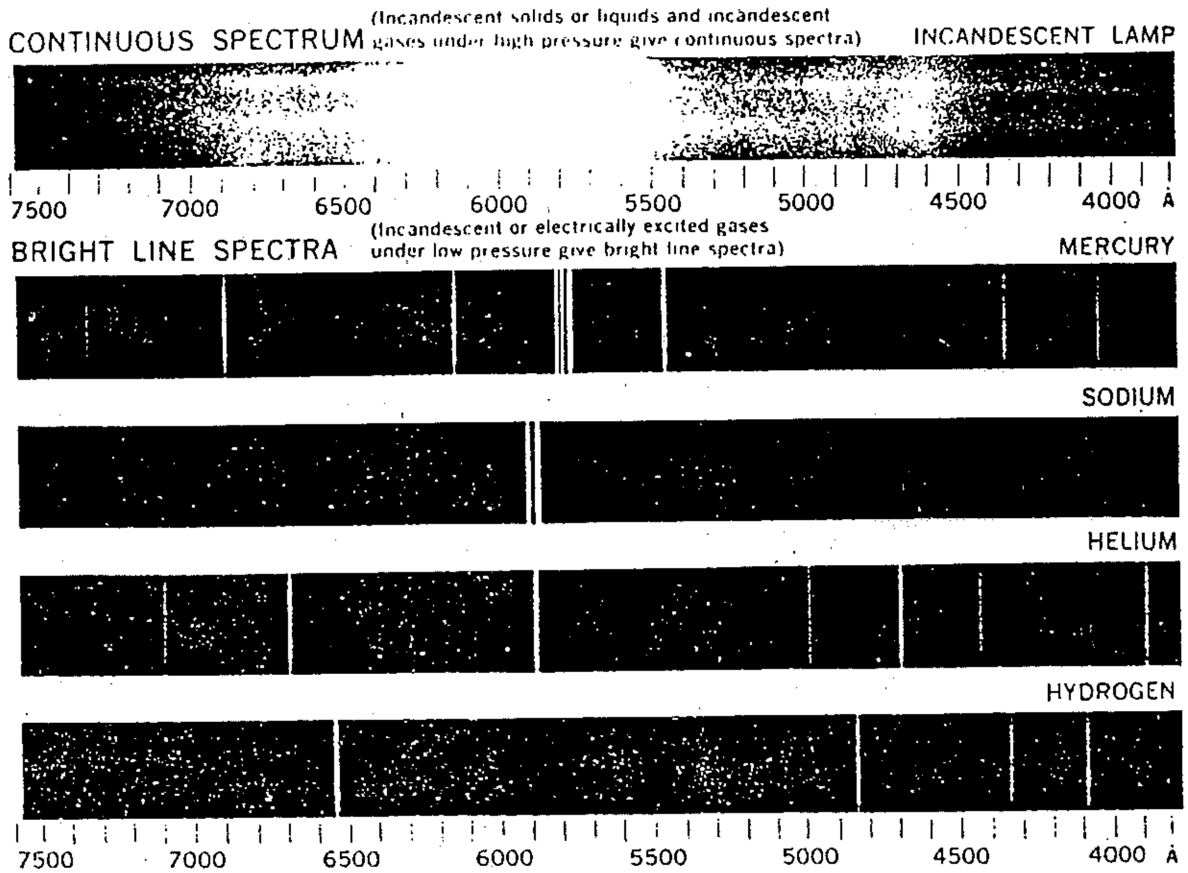
Each type of gas emits a characteristic set of wavelengths, called its spectrum.

Can be used for identification. [→ OH]

V2

OH

EMISSION SPECTRA



Adapted from the SPECTRUM CHART, Welch Scientific Company

DEMO: hand out diffraction gratings

close shutters, turn off lights

show:

- thermal spectrum from incandescent bulb (again)
- mercury [used in fluorescent lamps]
- [talk about sodium yellow light used in parking lots]
- helium [first discovered in sun's atmosphere]
- neon [used in neon signs]
- hydrogen

Hydrogen Balmer series

(red)	656 nm	H_α
(aqua)	486 nm	H_β
(blue)	434 nm	H_γ
(violet)	410 nm	H_δ

[story of Balmer, swiss math teacher]

Balmer guessed a formula for these wavelengths

$$\lambda = (\text{const}) \left(\frac{4n^2}{n^2-4} \right)$$

for integers n

$$\begin{cases} H_\alpha : n=3 \\ H_\beta \quad n=4 \\ H_\gamma \quad n=5 \\ H_\delta \quad n=6 \end{cases}$$

$\Rightarrow$ (const) $= 91.15\,nm$

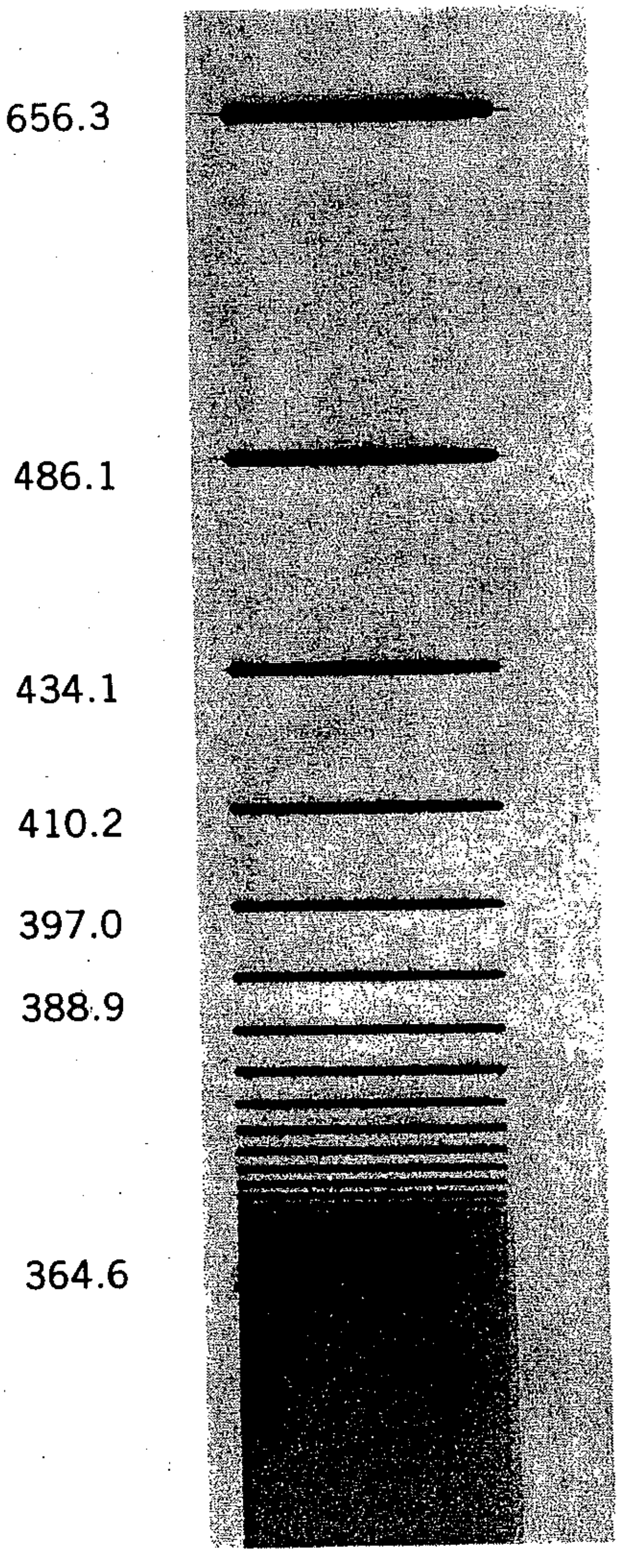
[What happens for $n=7$ & above?
Predictions for new lines of λ in the ultraviolet
Can't see them by eye but can photograph them

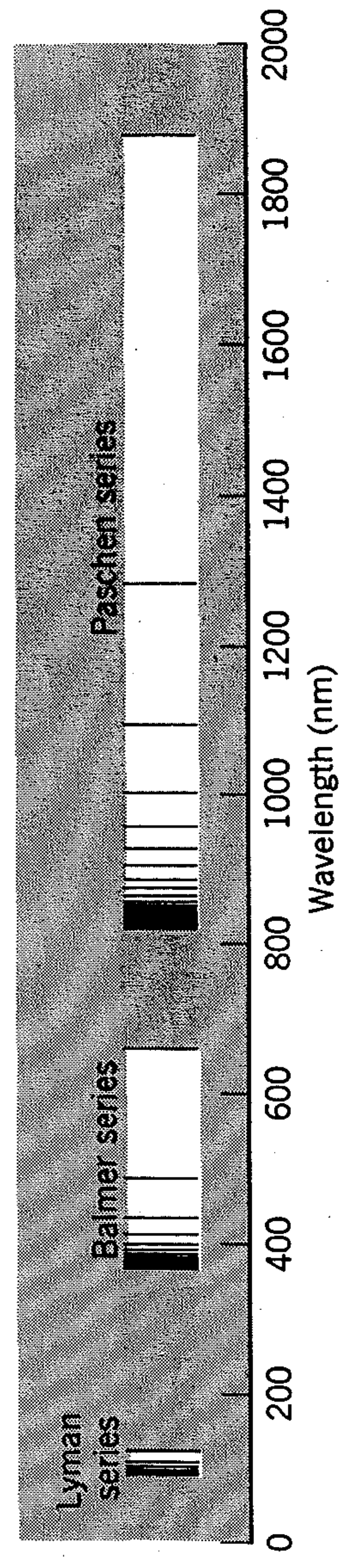
→ show transparency.

They are there! Process of science:
make predictions, then test them]

V5

011





HRK, ch 51, fig 1 and fig 2

$$\frac{1}{\lambda} = \frac{1}{(\text{const})}\left(\frac{n^2-4}{4n^2}\right) = \frac{1}{(\text{const})}\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

Rydberg proposed a more general formula

$$\boxed{\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)}$$

$R =$ Rydberg const $= 1.097 \times 10^7\ m^{-1}$

m, n different integers w/ $m < n$

$m = 1 \Rightarrow \frac{1}{\lambda} = R\left(1 - \frac{1}{n^2}\right),\ n = 2, 3, \ldots$ Lyman series (UV)

[see transparency]

$m = 2 \Rightarrow$ Balmer series

$m = 3 \Rightarrow \frac{1}{\lambda} = R\left(\frac{1}{9} - \frac{1}{n^2}\right),\ n = 4, 5, \ldots$ Paschen series (IR)

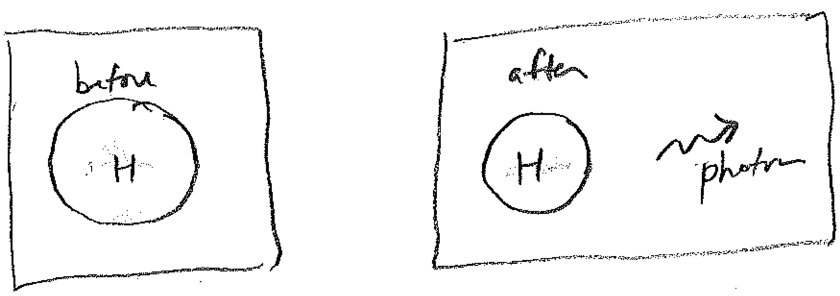
Quantum hypothesis: spectral lines of wavelength λ correspond to photons of energy

$$E_{photon} = hf = \frac{hc}{\lambda} = hcR\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

$$hcR = 13.6\ eV$$

If these photons are emitted by excited hydrogen atoms energy conservation says

$$E_{photon} = E_H^{before} - E_H^{after}$$



This suggests that hydrogen atoms have discrete energy levels

$$E_n = -\frac{hcR}{n^2}, \quad n = 1, 2, 3$$

[Negative because $U = K\frac{q_1 q_2}{r} = -\frac{Ke^2}{r}$]

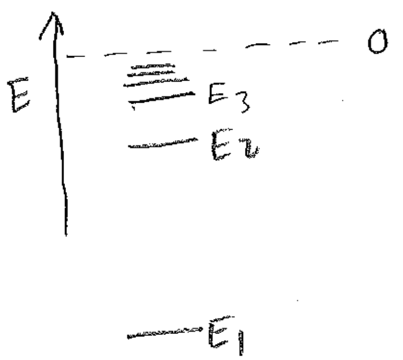
$$E_{photon} = E_n - E_m$$

n = initial state

m = final state

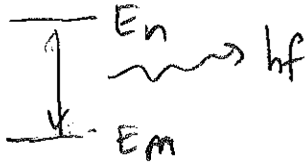
The lowest energy level of hydrogen ($n=1$) is called the ground state: $E_1 = -hcR = -13.6\,eV$.

Higher energy levels ($n \geq 2$) are called excited states and range from $E_2 = -\frac{13.6\,eV}{4} \approx -3.4\,eV$ to just below zero.

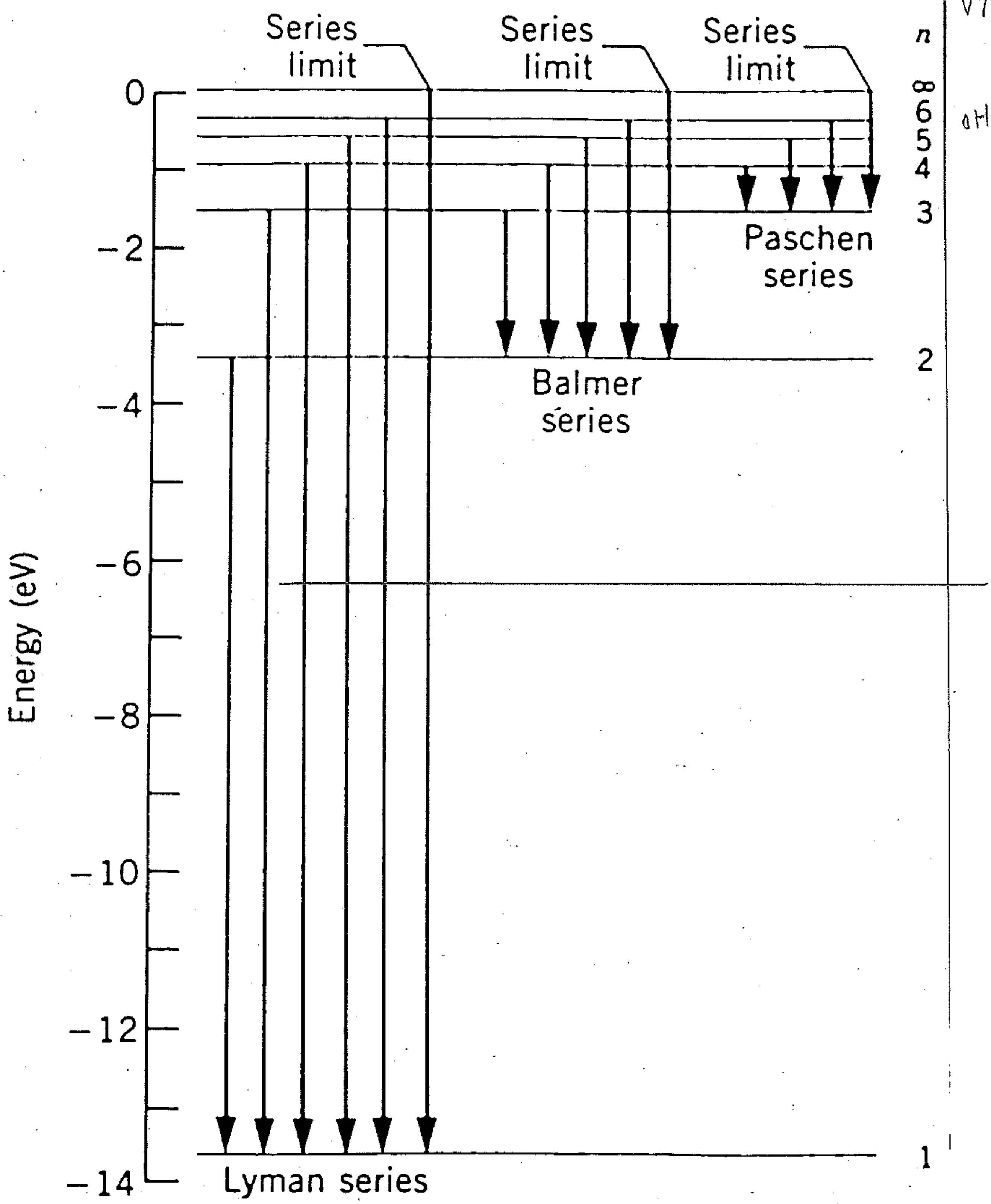


If $E \geq 0$, atom is ionized and the electron is free.

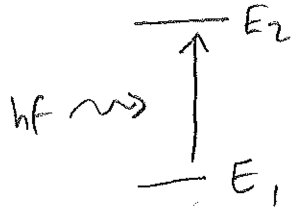
In a transition from level n to level m, an atom emits a photon whose energy is the <u>difference</u> of hydrogen energy levels



$$hf = E_n - E_m$$


Series limit
Series limit
Series limit
n
∞
6
5
4
3
2
1
0
−2
−4
−6
−8
−10
−12
−14
Energy (eV)
Paschen series
Balmer series
Lyman series
V9
oH

An atom in the ground state cannot emit light
but it can absorb a photon
whose energy is sufficient to reach an excited state



Since $E_2 - E_1 \approx -3.4\,eV - (-13.6\,eV) \approx 10\,eV$

we require $hf \gtrsim 10\,eV$

$$\Rightarrow \lambda = \frac{c}{f} = \frac{hc}{hf} < \frac{1240\,nm\cdot eV}{10\,eV} \sim 124\,nm$$

(UV light!)

Hydrogen gas is transparent to visible light
but can absorb ultraviolet

Similarly w/ other gases (N_2, O_2, ozone $= O_3$)
which thus absorb harmful UV radiation
from the sun

Other gases also have discrete energy levels

but there is no simple formula for them

[OH w/ mercury spectrum →]

They are experimentally determined using

$$E_{photon} = E_{atom}^{before} - E_{atom}^{after}$$

mercury has lines in the visible region

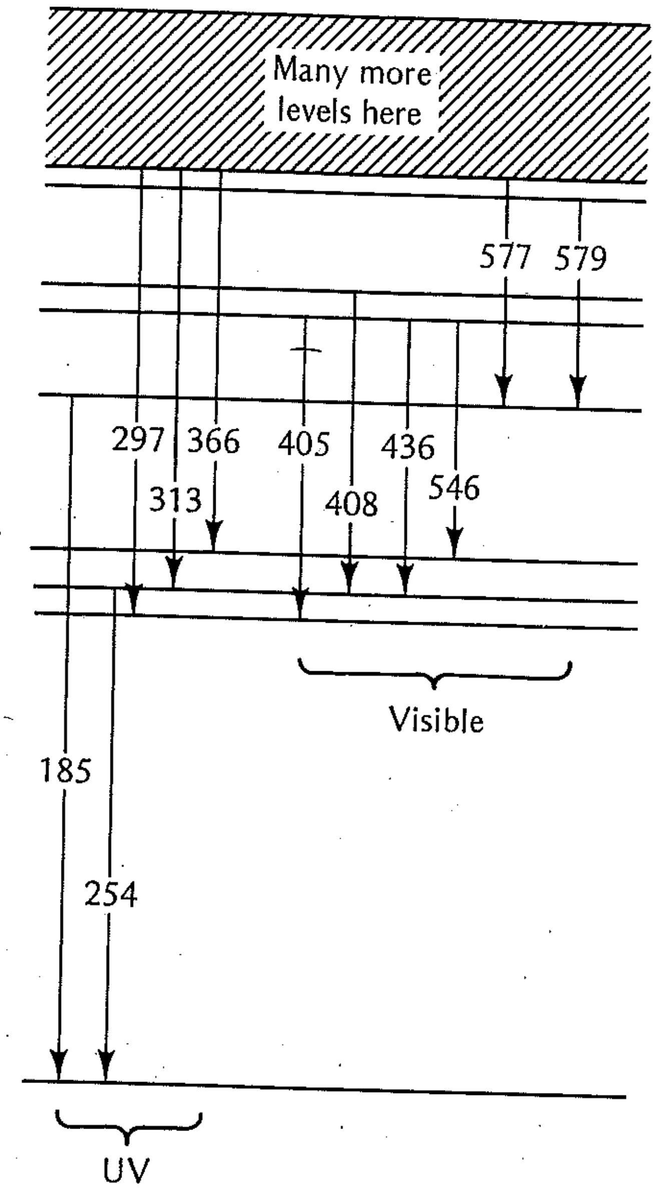
436 nm (blue)
546 nm (green)
578 nm (yellow)

but also in the ultraviolet

254 nm

366 nm

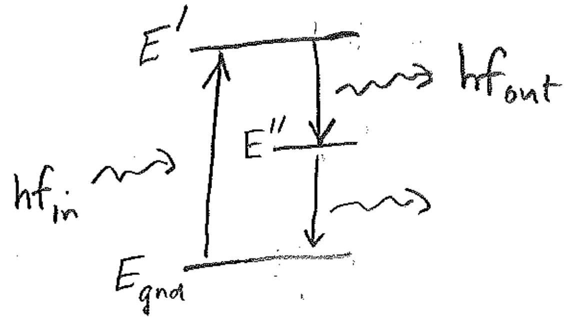
UV is absorbed by glass.



Mercury vapor energy levels

Fluorescence

process by which an atom in the ground state absorbs a photon of wavelength λ_{in} and subsequently emits a photon of wavelength λ_{out}



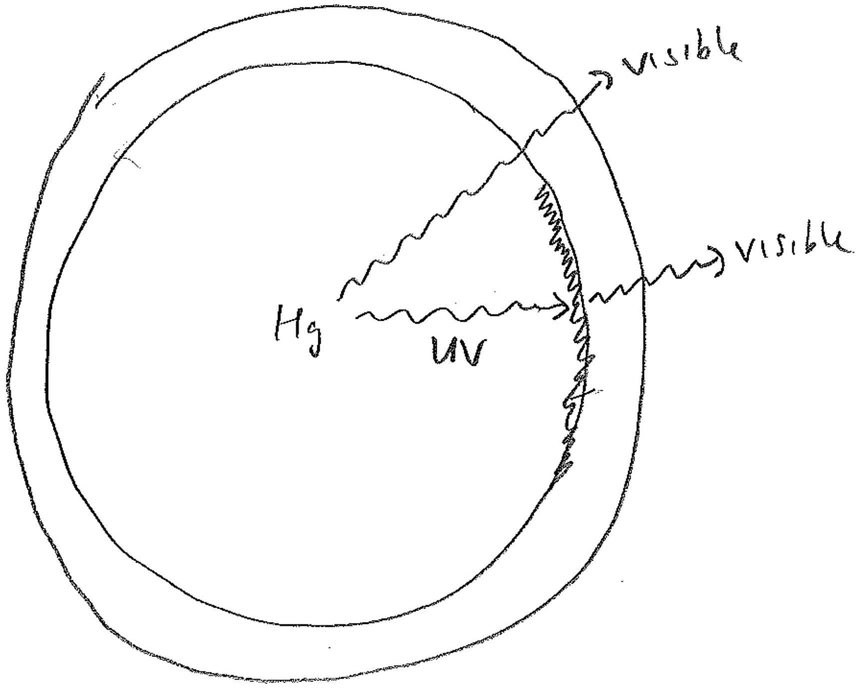
[which is larger: λ_{in} or λ_{out}?]

$$E' - E_{gnd} > E' - E''$$
$$hf_{in} > hf_{out}$$
$$\lambda_{in} < \lambda_{out}$$]

In this process, UV light can be converted to visible light

Fluorescent lamp

[excited Hg atoms emit both visible (bluish)
and UV light.
The UV is absorbed by the glass and
by a fluorescent coating on inside]



The coating re-emits light in the visible (white)

DEMO: half-coated fluorescent;
UV lamp on broken tube;
quinine water