4 - Line intensities and excited-state lifetimes

- So far, we have looked at whether a transition from an initial state a to a final state b is allowed or forbidden
- we are now interested in the relative intensities of these transitions

(*) Oscillator strength

$$f_{ka} = \frac{2m\omega_{ka}}{3\hbar} |\vec{r}_{ka}|^2 \quad , \text{with} \quad \omega_{ka} = \frac{E_k - E_a}{\hbar}$$

- <u>Physical</u> <u>interpretation</u>. that fraction of energy in the classical oscillator ascribed to a given transition

  - <u>Absorption</u> : $f_{ka} > 0$
  - <u>Emission</u> $f_{ka} < 0$

(*) The sum rule (Thomas, Reiche & Kuhn)

The sum of oscillator strengths over all states (including the continuum) is one.

$$\boxed{\sum_k f_{ka} = 1}$$

Below we will consider the components f_{ka}^x, f_{ka}^y, f_{ka}^z in the proof of this rule.

<u>Proof</u> : Let f_{ka}^x be defined as $f_{ka}^x = \frac{2m\omega_{ka}}{3\hbar} |x_{ka}|^2$

$$f_{ka}^x = \frac{2m\omega_{ka}}{3\hbar} \langle \psi_a | x | \psi_k \rangle \langle \psi_k | x | \psi_a \rangle$$

Using the Heisenberg equation $\dot{x} = \frac{1}{i\hbar}[x, H_0] = \frac{p_x}{m}$ yield

$$x_{ka} = \langle \psi_k | x | \psi_a \rangle = \frac{-i}{m\omega_{ka}} \langle \psi_k | p_x | \psi_a \rangle$$

$$x_{ak} = \langle \psi_a | x | \psi_k \rangle = \frac{i}{m\omega_{ka}} \langle \psi_a | p_x | \psi_k \rangle$$

$$\Rightarrow \quad f^x_{ka} = \frac{2i}{3\hbar} \langle \psi_a | p_x | \psi_k \rangle \langle \psi_k | x | \psi_a \rangle$$

$$= -\frac{2i}{3\hbar} \langle \psi_a | x | \psi_k \rangle \langle \psi_k | p_x | \psi_a \rangle$$

$$= \frac{i}{3\hbar} \Big[\langle \psi_a | p_x | \psi_k \rangle \langle \psi_k | x | \psi_a \rangle - \langle \psi_a | x | \psi_k \rangle \cdot$$

$$\times \langle \psi_k | p_x | \psi_a \rangle \Big]$$

we are interested in $\sum_k f^x_{ka} = \frac{i}{3\hbar} \sum_k \Big[\langle \psi_a | p_x | \psi_k \rangle \langle \psi_k | x | \psi_a \rangle$

$$- \langle \psi_a | x | \psi_k \rangle \langle \psi_k | p_x | \psi_a \rangle \Big]$$

Using the closure relation $\sum_k |\psi_k\rangle\langle\psi_k| = I$ we have

$$\sum_k f^x_{ka} = \frac{i}{3\hbar} \langle \psi_a | \underbrace{p_x x - x p_x}_{[p_x, x] = -i\hbar} | \psi_a \rangle$$

$$\Rightarrow \sum_k f^x_{ka} = \frac{1}{3} \quad (*)$$

Similarly, $\sum_k f^z_{ka} = \frac{i}{3\hbar} \langle \psi_a | [p_z, z] | \psi_a \rangle = \frac{1}{3} \quad (**)$

$$\sum_k f^y_{ka} = \frac{i}{3\hbar} \langle \psi_a | [p_y, y] | \psi_a \rangle = \frac{1}{3} \quad (***)$$

$$(*) + (**) + (***) = \sum_k f_{ka} = 1$$

- **Hydrogenic atoms:** The bound-state wavefunctions $\psi_{n\ell m}(\vec{r}) = R_{n\ell}(r)\, Y_\ell^m(\theta, \varphi)$ are known exactly This implies that the oscillator strengths are easy to compute

  In this case, the labels k, a refer to all the quantum numbers of the system.

Average oscillator strength (transition $n\ell \to n'\ell'$)

$$\bar{f}_{n'\ell', n\ell} = \frac{1}{2\ell+1} \sum_{m'=-\ell'}^{\ell'} \sum_{m=-\ell}^{\ell} f_{n'\ell'm', n\ell m}$$

- **Transition rates for spontaneous emissions**

$$W_{ka}^{s,D} = \frac{2\hbar\alpha}{mc^2}\, \omega_{ka}^2\, |f_{ka}|$$

4.(b) - Atomic lifetimes

Let us consider N(t) atoms in an excited state b at a particular time t. The rate of change of N(t) is

$$\frac{dN(t)}{dt} = -N(t) \sum_k W_{kb}^{s} \qquad (****)$$

↳ sum over all states k to which decay is allowed.

Integrating (****), $N(t) = N(t=0)\, \exp(-t/\tau_b)$, where

$$\tau_b^{-1} = \sum_k W_{kb}^{s}$$

τ_b is called the lifetime of the level b

⊛ Please note :

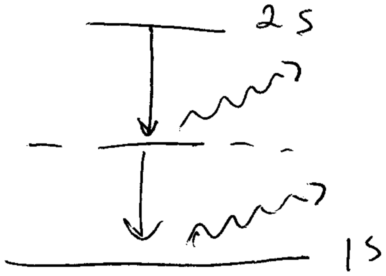
- In the absence of external fields, the lifetime of an atom cannot depend on the magnetic quantum number m of the level b.

- The lifetimes of hydrogenic ions are shorter than those in hydrogen and are given by the scaling laws

$$\tau(Z) = Z^{-4}\,\tau(Z=1)$$

- In the dipole approximation, the lifetime of 2s in Hydrogen is infinite

(In practice, $\tau_{(2s)} \sim \frac{1}{7}$ s, and the transition 2s → 1s occurs by the emission of 2 photons)



5 - Measurements of radiative lifetimes

- Importance of oscillator strengths (f-values) of spectral lines: computation of gas discharges, plasmas, stellar atmosphere, etc.

- In general, theoretical predictions are not accurate: experimental measurements are necessary

⊛ Direct methods: f can be determined through the intensity of the spontaneous emission of a given Spectral line

$$I_{ki} \propto \underbrace{A_{ki}}_{\text{transition probability}} \overset{\text{density}}{N} \underset{\text{volume}}{V} \hbar\omega_{ki}$$

- **Problem**: in many cases, the density cannot be determined accurately

  $\Rightarrow$ absolute f-value measurements are gener inaccurate

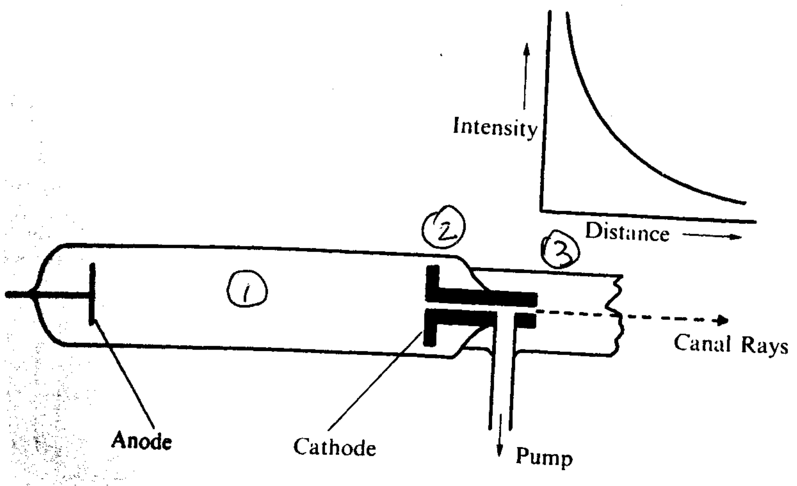
- **Solution**: f is normally determined by measuring radiative lifetimes

  Examples: beam-foil method, delayed coincidence method,

5.(a) - The beam-foil method

⊛ **Key idea**: "The time-dependent exponential decay of excited atoms may be converted into a spatial variation of intensity by exciting a beam of fast-moving atoms at a given position

⊛ **Early set-ups**: Wien (1927); canal ray method



Corney, Atomic & Laser spectroscopy, P. 145

① Positive ions are accelerated

② Excited atoms capture e^-s by charge - e^- collisions

③ Moving atoms decay - a faint glow is emitted
⇒ The length of the glow allows the radiative lifetime to be measured if the velocity of the atoms can be estimated

<u>Problem</u> : repopulation of the excited states by radiative decay from higher levels ⇒ leads to too long lifetimes
Overcome by Koenig + Ellett (1932) using optical excitation instead of collisions
(restricted to lifetimes > 10^{-6} s due to the low velocity of the beam)

(*) <u>Modern</u> <u>technique</u>

- Based on the fact that ions in the beam of a Van de Graaf accelerator can be strongly excited by passing through a thin carbon foil (Kay, 1963 ; Bashkin, 1964).

• Advantage: high velocity (10^8 cm/s) ⇒ radiative decay extends over several cms.

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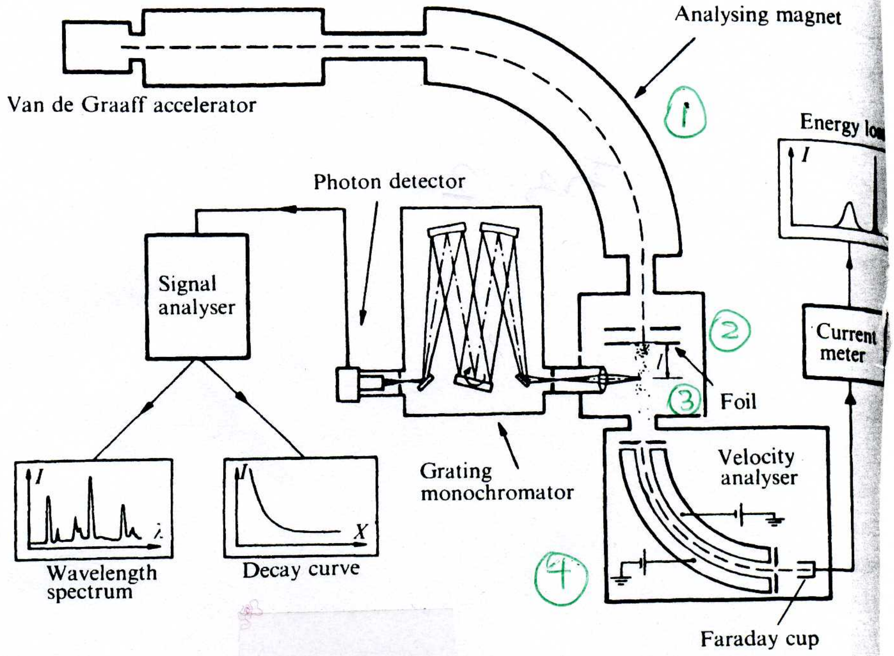


① Acceleration of ions – initial velocity spread determined by the analyzing magnet

② Ions collide with the foil: excitation..

③ Ions decay: intensity / wavelength of the emitted radiation is detected

Advantages:

* Low pressure – collisions or radiation trapping are not important
* Wide range of applications: most light and medium heavy elements can be excited. This technique is also applicable to molecular ions
* High chemical purity: simplifies the classification of spectral lines.
*

④ Calibrating of beam velocity: one must take into account the energy loss of the ions passing through the foil.

- Calculation of lifetimes

$$\underset{\substack{\downarrow \\ \text{density} \\ \text{of ions} \\ \text{@ position } l}}{N_k(l)} = \underbrace{N_k(0)}_{\substack{\downarrow \\ \text{density of ions @ the downstream face of the} \\ \text{foil}}} \exp(-t/\tau_k) \qquad t = l/v$$

$\ln N_k(l)$ is plotted as a function of l ⇒ slope gives τ_k

- Easier to analyze the numbers of ions decaying between l and $l + \Delta l$

$$N(l, \Delta l) = N_k(0) \exp\left[-\frac{l}{v\tau_k}\right]\left[1 - \exp\left[\frac{-\Delta l}{v\tau_k}\right]\right] \underbrace{S\,\Delta l}_{\text{volume of the region}}$$

~~Diff~~

- **Problem** : radiative cascade : the plot shows a pronounced curvature due to the repopulation of the level being studied by the decay from higher-lying levels.

Remember : the ions are excited by collisions and this is an unselective process

The radiative cascade can be avoided by replacing the foil by an intense laser ⇒ strict selection rules

5. (b) - The delayed coincidence method

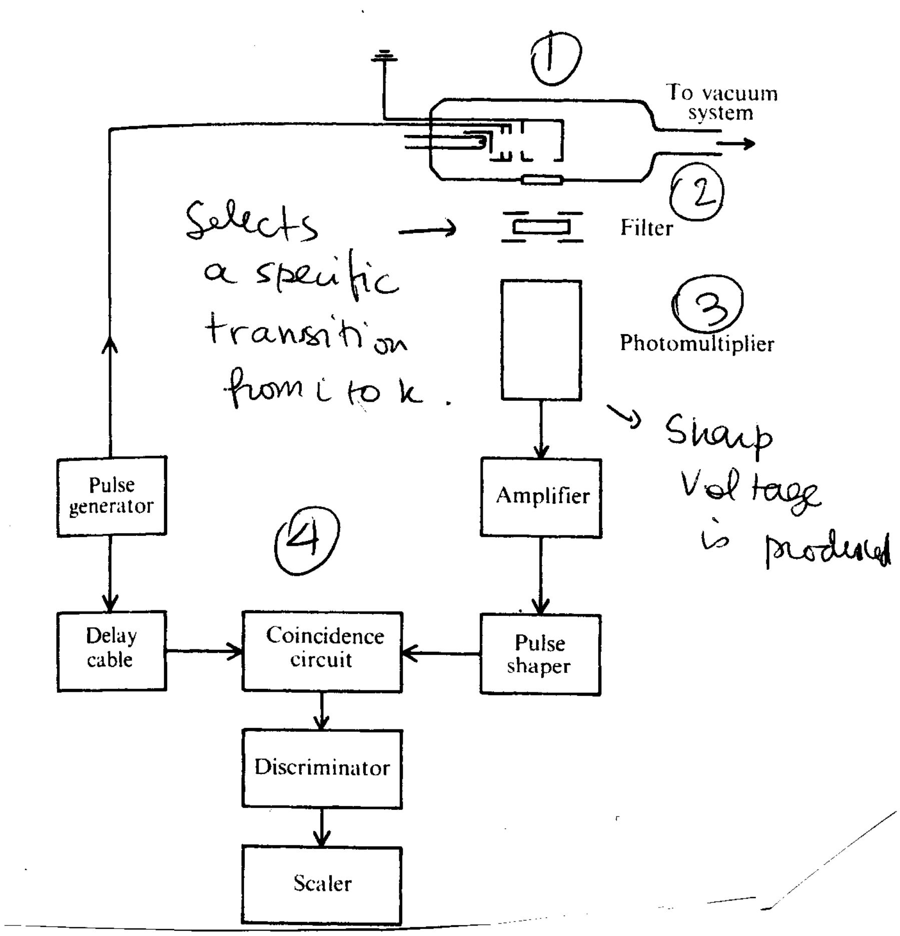
Heron et al, Nature 174, 564 (1954)

(*) key idea : ① A sample is excited to some level k

② The excitation is cut off instantaneously

③ The emitted photons produce a pulse in the detector - the number of pulses is detected.

④ Number of counts × delay time enables to determine τ_k.



Selects a specific transition from i to k.

Sharp Voltage is produced

Probability of detecting a photon ~~from~~ related to decay transition from k to i ~~[illegible]~~ in a time interval $[t, t+\Delta t]$ after the removal of the excitation:

$$P(t,\Delta t) \propto A_{ki}\, N_k(0)\, \exp(-t/\tau_k)\,\Delta t$$

④ Coincidence measurement: pulses from the detector are compared to the pulses from the e^- gun.

- Problems: ~~the light produced~~.
  - The detector is sensitive to photons arriving only with a specified short time interval following the excitation
  - The light produced has very low intensity

Solution: Multi-channel technique – the detector should be sensitive to photons arriving at *all* times after the removal of the excitation pulse.

Details: Chapter 6, A. Corney, Atomic and Laser spectroscopy

5(c) - The time of flight method

Van Dyck, et al, Phys Rev Lett. 25, 1403 (1970)

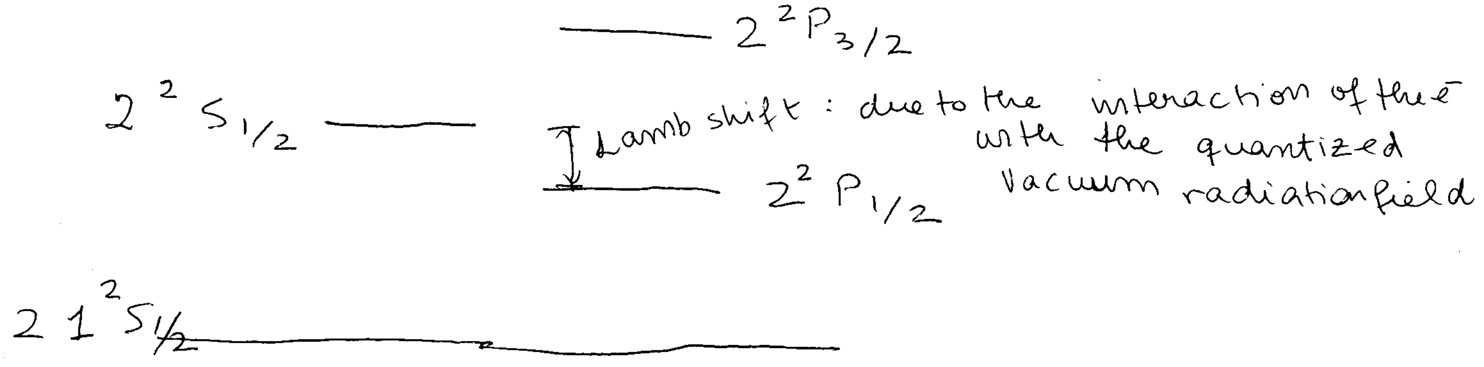
(*) Importance : this method is widely used for determining the lifetimes of metastable states

Typically, such times are $\tau > 10^{-3}$ s

(*) Problems with beam-foil/delayed coincidence method :

- Beam foil method: no decay would be observed for an apparatus of realistic size
- Delayed coincidence techniques: the time necessary for obtaining sufficient data is unrealistic

Example : Metastable states in He^+



- Reminder : spectroscopic notation: $n^{2S+1}A_j$

A ≡ letter associated with the

orbital quantum number l

$2S+1 \equiv$ multiplicity of the level

$J \equiv$ quantum number associated with the total angular momentu

$\vec{J}$.

$2^2P_{3/2}$ means that : $l = 1$
$S = 1/2$ and there is
$J = 1 + 1/2 = 3/2$ multiplicity 2
(two-fold degener

$2^2P_{1/2} \Rightarrow l = 1$
$S = 1/2$ two fold degenerate
$J = 1 - 1/2 = 1/2$

Let us now have a closer look at $2^2S_{1/2}$

(a) Transition $2^2S_{1/2} \rightarrow 2^2P_{1/2}$:

Electric dipole transitions are allowed, but probability is very small $\Rightarrow \tau \sim 163$ years.

(b) Transition $2^2S_{1/2} \rightarrow 1^2S_{1/2}$:

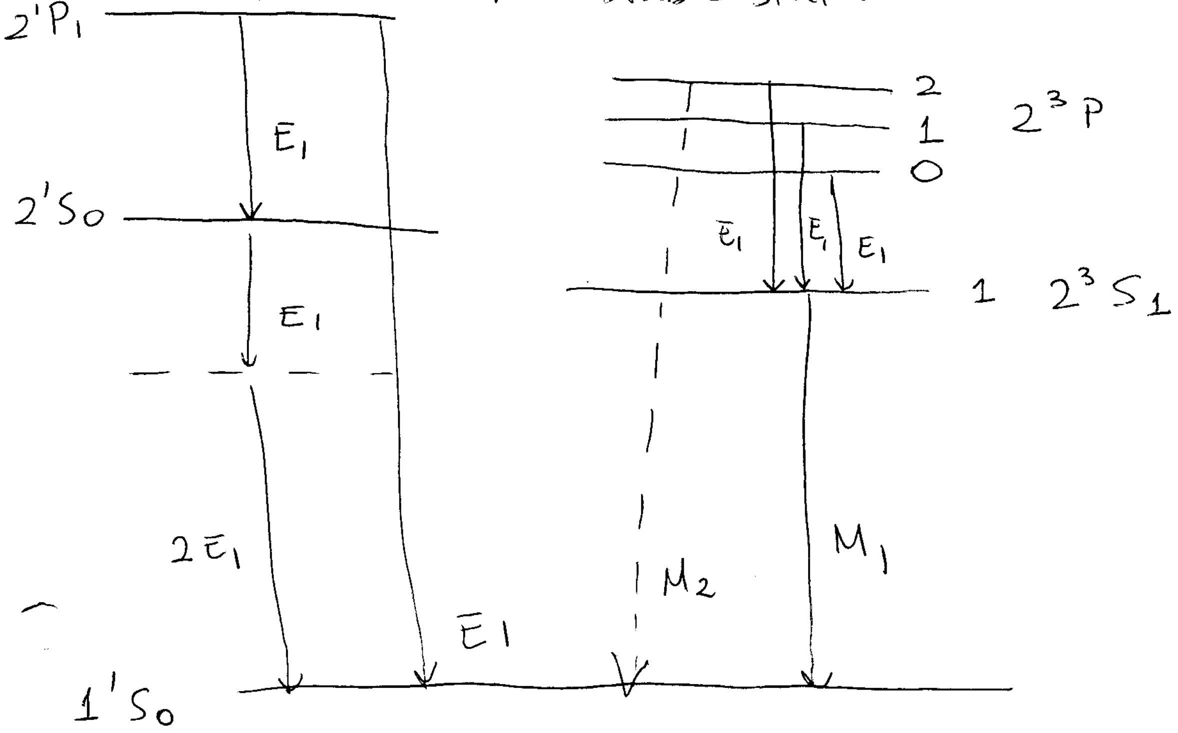
- Electric dipole:
  Forbidden by the dipole transition selection rules
  (same parity for both levels)
- Electric quadrupole:
  Since $J = 1/2$ for both levels this transition is also forbidden
- Magnetic quadrupole:
  Forbidden, as radial wavefunctions are orthogonal
  (Remember in this case one must compute

$$\int_0^\infty R_{21} R_{10} r^2 dr \quad)$$

with relativistic corrections to the magnetic dipole moment operator $\Rightarrow \tau \sim$ five days

(c) Most probable process: two-photon decay such that $\hbar\omega_1 + \hbar\omega_2 = E_k - E_i$ (Modelling: 2nd order perturbation theory) $\tau \simeq \frac{1}{7}$ s

Helium - Metastable states



See Corney, p. 204

- Decay $2^1S_0 \rightarrow 1^1S_0$: Different parity : Forbidden by electric dipole selection rules

$\Delta J = 0$, $J_i = 0$, $J_f = 0$: Forbidden by electric dipole / electric quadrupole selection rules

$\Delta J = 0$, $J_i = 0$, $J_f = 0$: Forbidden by magnetic dipole selection rules

Orthogonal radial wavefunction

Decay by relativistically assisted dipole transitions is possible, but improbable

$\Rightarrow$ 2^1S_0 is a metastable state

(*) Decay $2^3S_1 \rightarrow 1^1S_0$.

- Electric dipole transition: not allowed as levels have the same parity $\Delta l = 0$
- Electric quadrupole transition: not allowed since $\Delta J = 1$, $J_i = 1$, $J_f = 0$

- Magnetic dipole transition: in principle possible, but would violate $\Delta S = 0$.

This level is also metastable

Decay mechanism:

- Until the late 1960s it was believed to be a 2 photon dipole transition
- Gabriel + Jordan, Nature 221, 947 (1969) : spin-dependent relativistic corrections to the magnetic dipole operator (in the context of solar X Ray lines)

⊛ Time of flight method

① Atoms or molecules of the gas to be investigated pass through a cooled source chamber and effuse through a slot in a pumping region

② Electron gun excites them to the required metastable level

③ Metastable atoms/molecules enter a low pressure region

④ The gas collides with 2 targets:

(a) A 60% transparent copper mesh
(b) A copper plate

In (a) and (b) there exist electron multipliers that detect e⁻s ejected from the target by the metastable atoms.

⑤ The output pulses from (a) and (b) are recorded as functions of the time after the excitation (the distance of the targets from the excitation region are known)

⇒ Velocity distributions at each detector are determined.

One may determine the number of atoms which decay between both detectors by comparing the numbers of metastable atoms within a specific velocity intervals arriving at the detectors.

$$\underbrace{N_i(v)}_{\text{number of atoms at detector } i} = \int_{\text{surface}} \overset{\text{surface efficiency of detector } i}{\varepsilon_i}\; \underbrace{N_0(v)}_{\text{initial number of atoms}} \exp(-t_i/\tau)\, \underbrace{ds}_{\text{area of the detector}}$$

- If the initial velocity distribution is uniform across the beam

$$N_i(v) = \overbrace{\int_{\text{surface}} \varepsilon_i \, ds}^{C_i} \; N_0(v) \exp(-t_i/\tau)$$

Ratio of numbers of atoms at both detectors)

$$R = \frac{N_b(v)}{N_a(v)} = \frac{C_b}{C_a} \exp(-t/\tau)$$

$$t = t_b - t_a = \text{"time of flight"}.$$

(*) Specifically for He, there are 2 metastable levels: one can be eliminated by a lamp, which excites the atom to a close, non - metastable level. For instance, the excitation $2^1S_0 \to 2^1P_1$ can be induced: the transition is "quenched". By switching the lamp on and off one may compare the full results to those obtained in the presence of the lamp.