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CHM 301

1. Analytical Seperations
2. Molecular spectroscopy and flame methods
3. Luminescence, Nephelometry and Turbidimetry
4. Atomic ~~structure~~ Spectra and spectra line waves
5. Analytical Automation.

Introduction to Spectro~~metry~~ry

Spectrometry
It is the interaction of energy with ~~matter~~

Spectrophotometry is the interaction of light energy with matter.

instrument: spectrophotometer

Spectrophotometric methods are large group of analytical methods that are based on atomic and molecular spectroscopy. Spectroscopy is the science that deals with the interaction of various types of radiation with matter; usually between electromagnetic radiation and matter. But, could also include radiations between matter and other form of energy such as acoustic waves, and beams of Particles (ions and electrons)

Spectrometry and spectrometric method refers to the measurement of intensity ~~of radiation~~ with a photoelectric transducer or other types types of electronic devices.

Energy state of Chemical Species

Some of the important postulate of quantum theory that can be used to explain interactions of radiation and matter are:

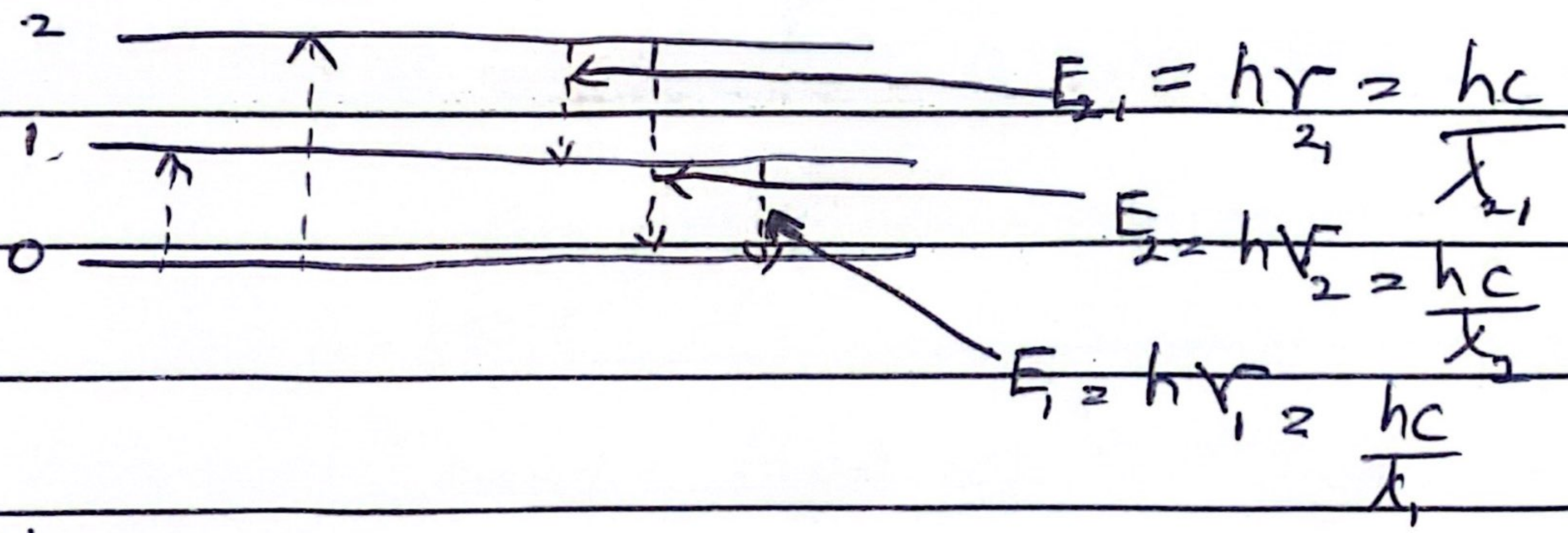
(1) atoms, ions and molecules can exist only in certain discrete states, characterized by definite amount of energy

(2) When a species changes its state, it absorbs or emit an amount of energy exactly equal to the energy difference between the states

(3) When atoms, ions or molecules absorb or emit radiation, in making a transition from one energy state to another, the frequency ν or the wavelength λ, of the radiation is related to the energy difference between the states by the equation;

$$E_1 - E_0 = h\nu = \frac{hc}{\lambda}$$

Where, E_1 is the energy of the higher state
E_0 " " " of the lower state
C is the speed of light
h is the planck's Constant (6.626×10^{-34} Js)



Note: For atoms or ions in the elemental state, the energy of any given state arise from the motion of electrons around the positively charged nucleus, hence, the various energy state are called the electronic state. Molecules also have quantized vibrational states that are associated of the inter atomic vibrations and quantized rotational state that arise from the rotation of molecules around their center of mass.

The lowest energy state of an atom or molecule is its ground state, while their higher energy state are term exited state. Usually, at room temperature, chemical species are at their ground state.

12-11-2024

Acquiring Information About an Analyte

When a sample or analyte is stimulated by applying energy in the form of heat, electrical energy, light, particles bombardment or a chemical reaction or a chemical reaction. Some of the analyte species undergo a transition from their ground state to the excited state.

Information about the analyte's identity and concentration is aquired by measuring the electromagnetic radiation

emitted as it returns to the ground state or by measuring the amount of electromagnetic radiation absorbed or scattered as a result of excitation.

The result of such a measurement are often expressed graphical spectrum, which is a plot of the emmitted radiation as a function of frequency or wavelength.

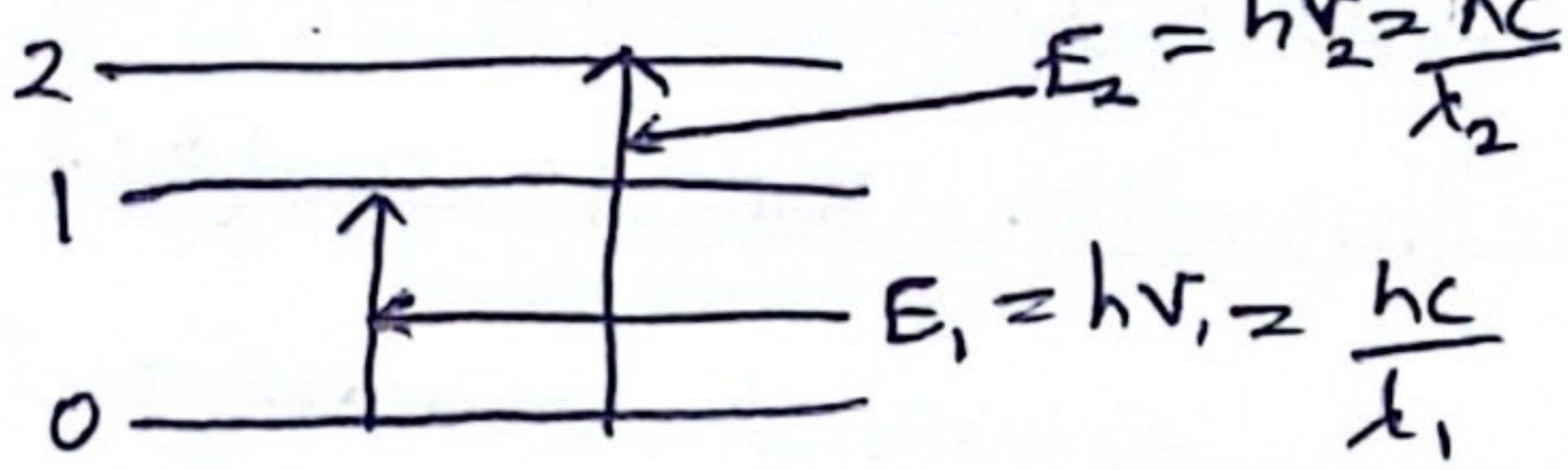
When the sample is stimulated by the application of an external electromagnetic radiation source, the radiation can be reflected, scattered or absorbed

(i) Absorption Method

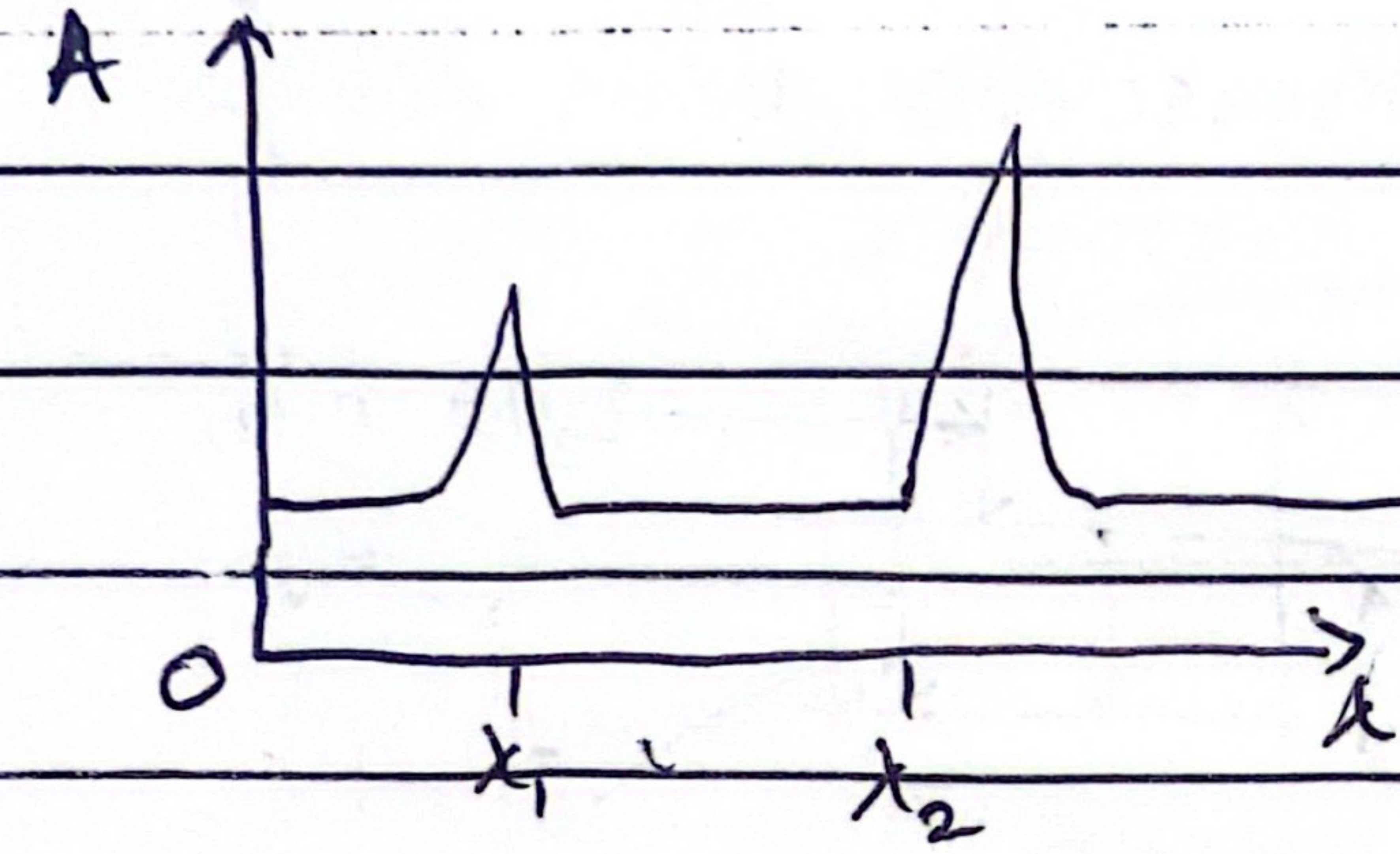
Radiation of incident radiant power P_0 can be absorbed by the analyte resulting in a transmitted beam of lower radiant power P.

For absorption to occur, the energy of the radiation beam correspon to one of the energy differences shown in (b) and (c)

(a)



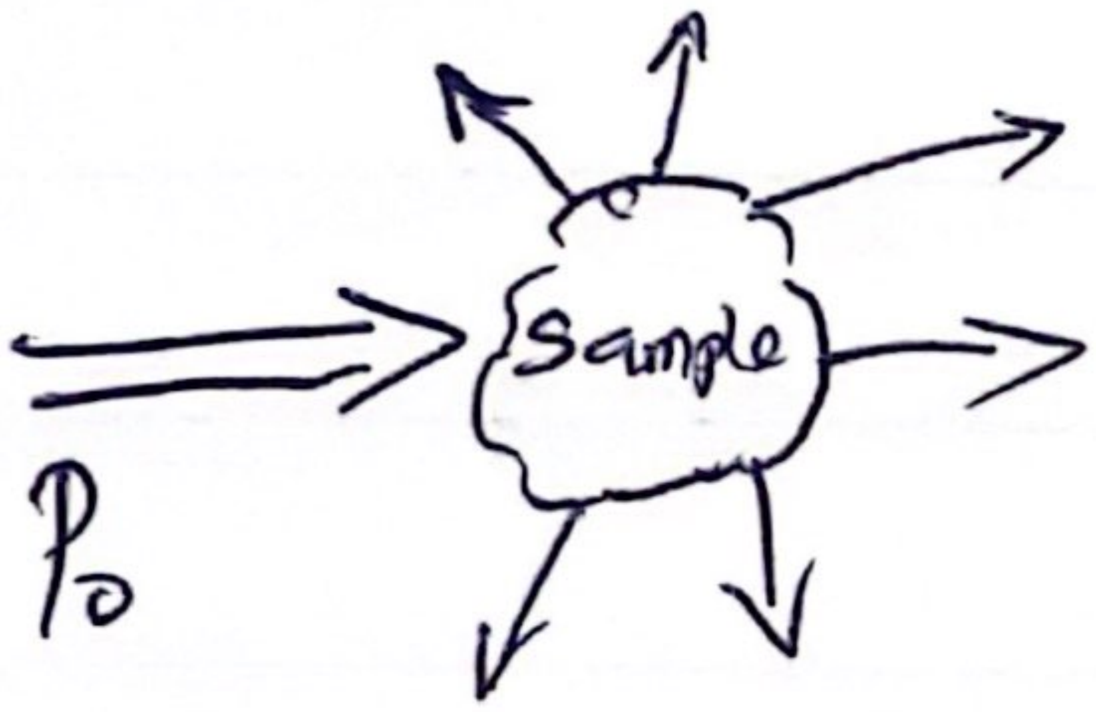
(b)



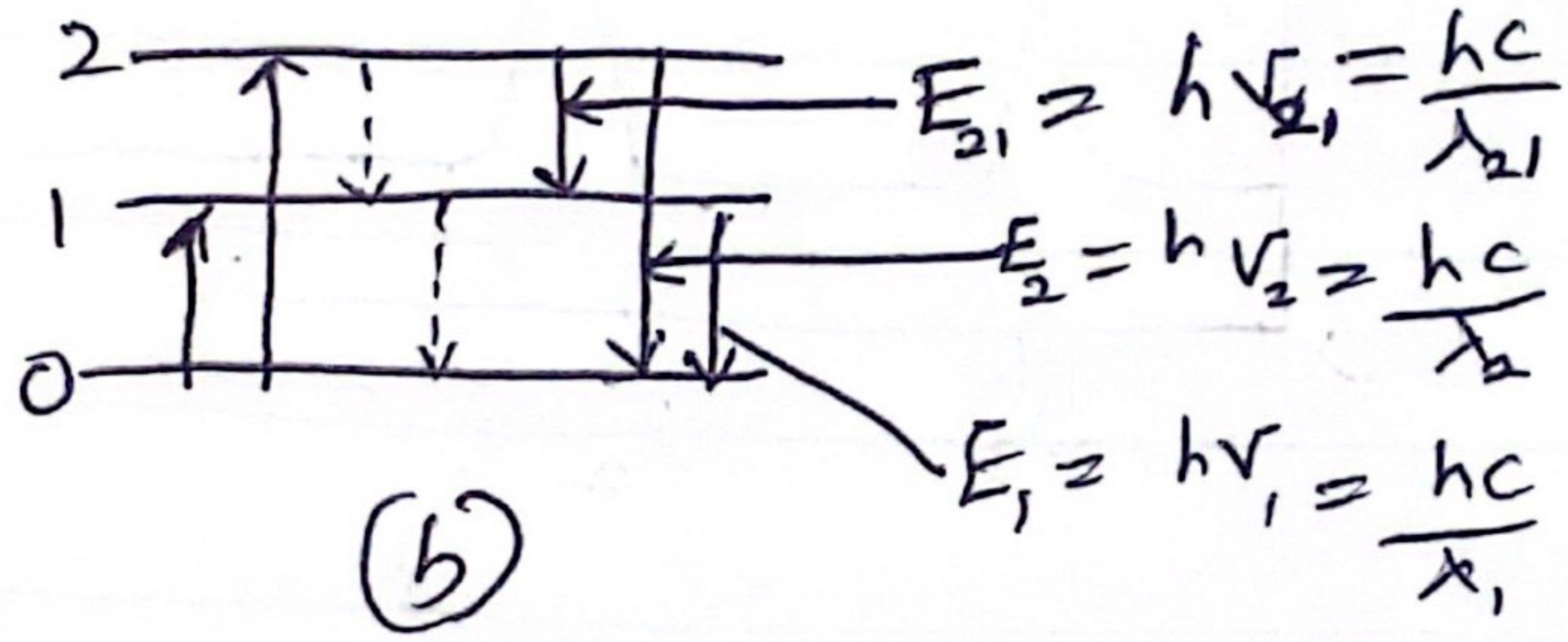
(2) Photoluminescence Methods

Fluorescence and phosphorescence results from absorption of electromagnetic radiation and then dissipation of the energy emission of radiation

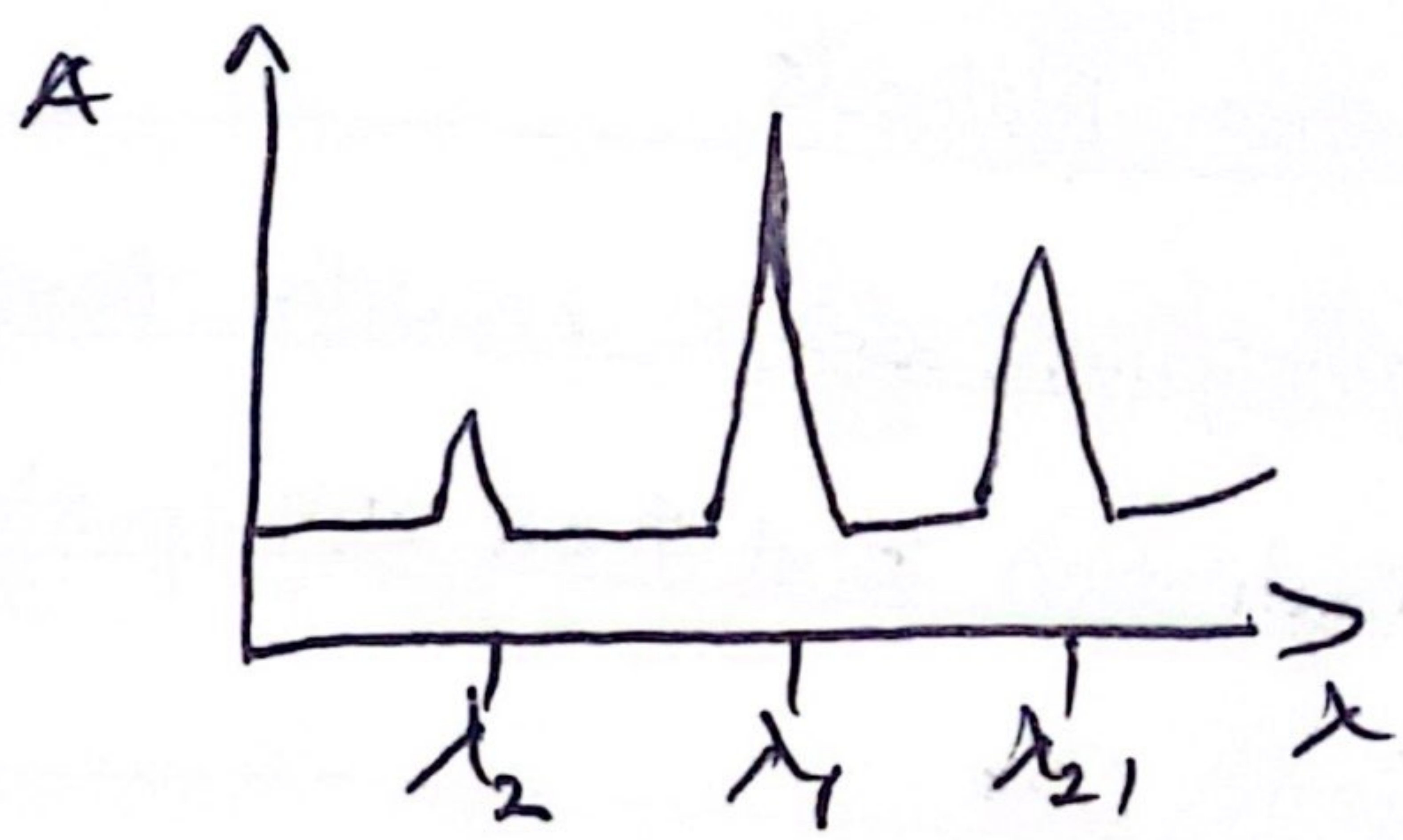
(a) In (b), the absorption can cause excitation of the analyte to state 1 or state 2. Once excited, some energy can be lost by emission of a photon (luminescence), shown as solid lines or by non radiating process, dashed lines. The emission occurs over all angles (scattered radiation), and the wavelengths emitted is seen corresponds to energy difference between levels. The major distinction between fluorescence and phosphorescence is the time scale of emission; with fluorescence being prompt and phosphorescence being delayed.



(a)



(b)



(c)

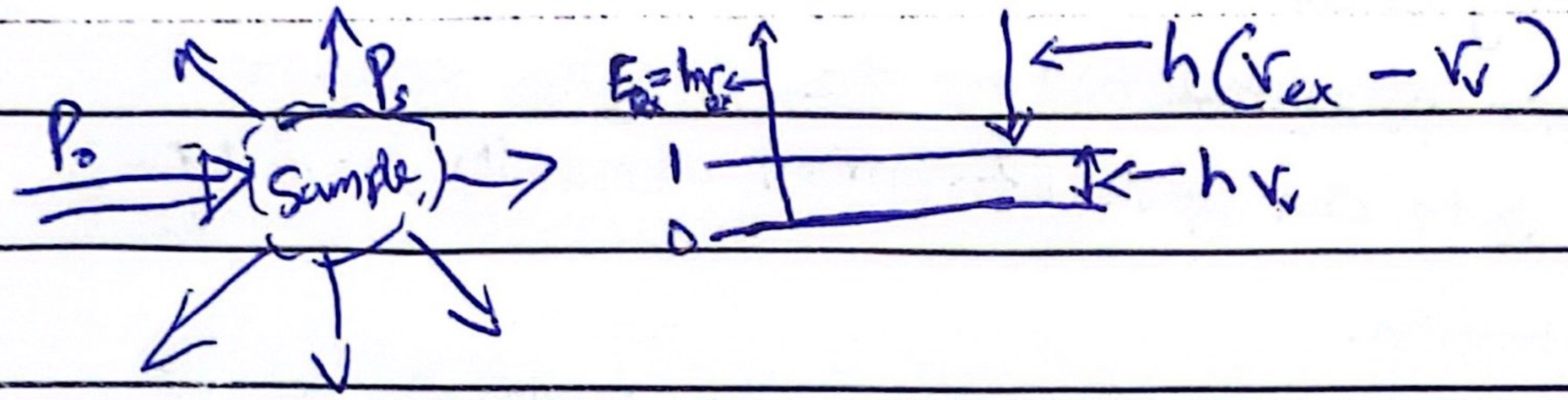
③ Scattering of Radiation

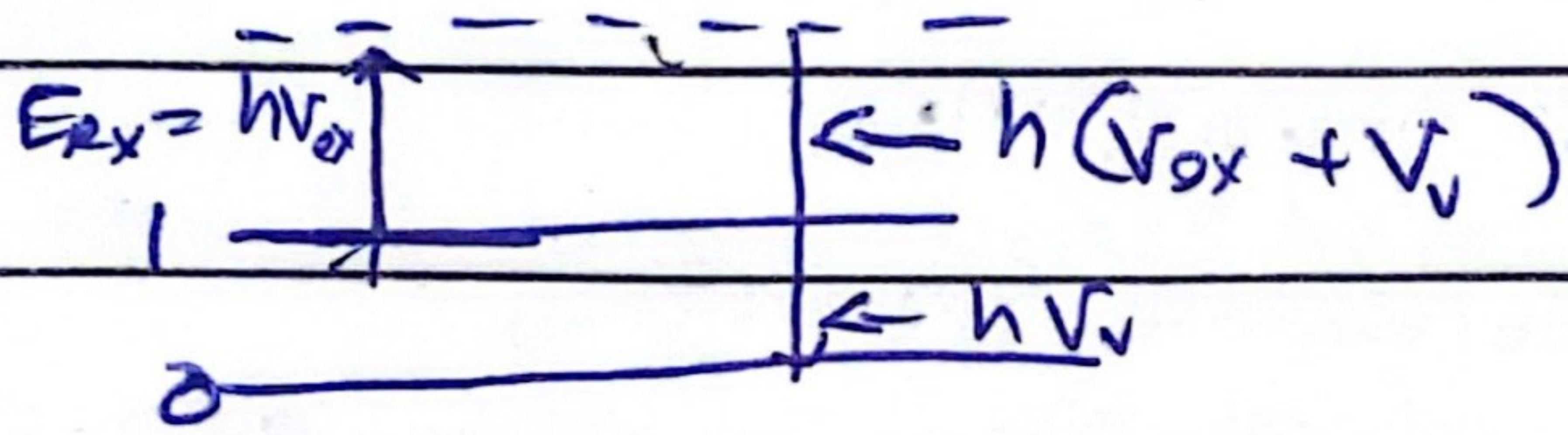
When radiation is scattered, the interaction of the incoming radiation ~~woul~~ with the sample maybe elastic or inelastic.

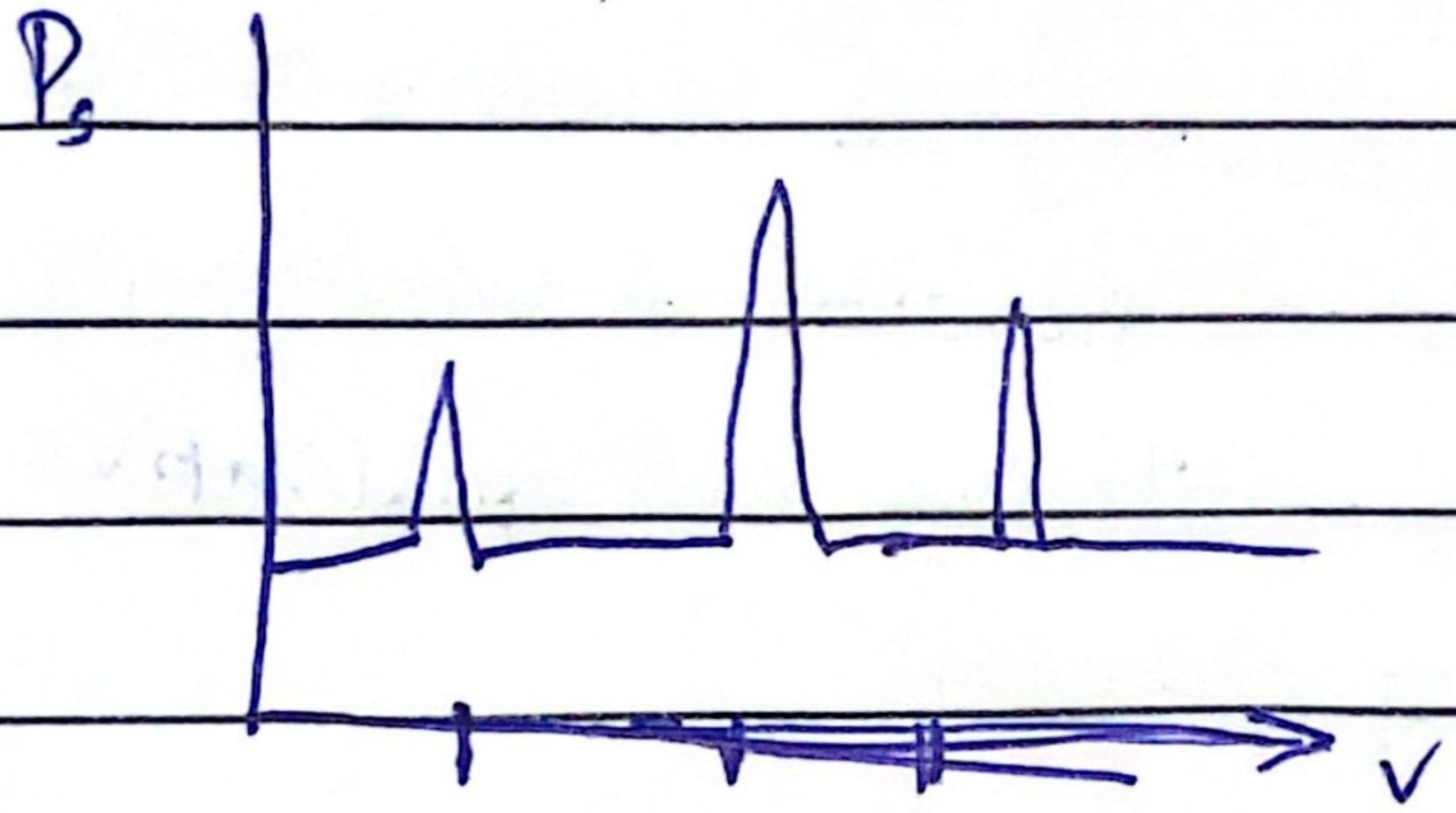
In elastic scattering, the wavelength of the scattered radiation is the same as that of source radiation.

The intensity of the elastically scattered radiation is used to make measurement nephelometry and turbidimetry and particle sizing

14th November 2024







Classes of Spectroscopy

There are two major classes of spectroscopy namely:

(i) Emission spectroscopy (ii) Absorption spectroscopy

Emission spectroscopy involves methods in which the stimulus is the heat or electrical energy

Chemiluminiscene spectroscopy refers to excitation of the analyte by chemical reaction. In both cases, measurement of the radiant powe emitted as the analyte returns to the ground state can give information about its Identity and concentration.

In photoluminiscence spectroscopy the emission of the Photons is measured after absorption.

Fluorescence and phosphorescence Spectroscopy are the most importance forms of pholuminsscence

In absorption spectroscopy we measure the amount of light absorbed as the function of wavelength. This can give both quantitative and qualitative information about the spectroscopy

Emission of Radiation

Electromagnetic radiation is produced when excited particles such as atoms, ions or molecules relax to lower energy levels by given up their excess energy as photons

Excitation can be brought about by;

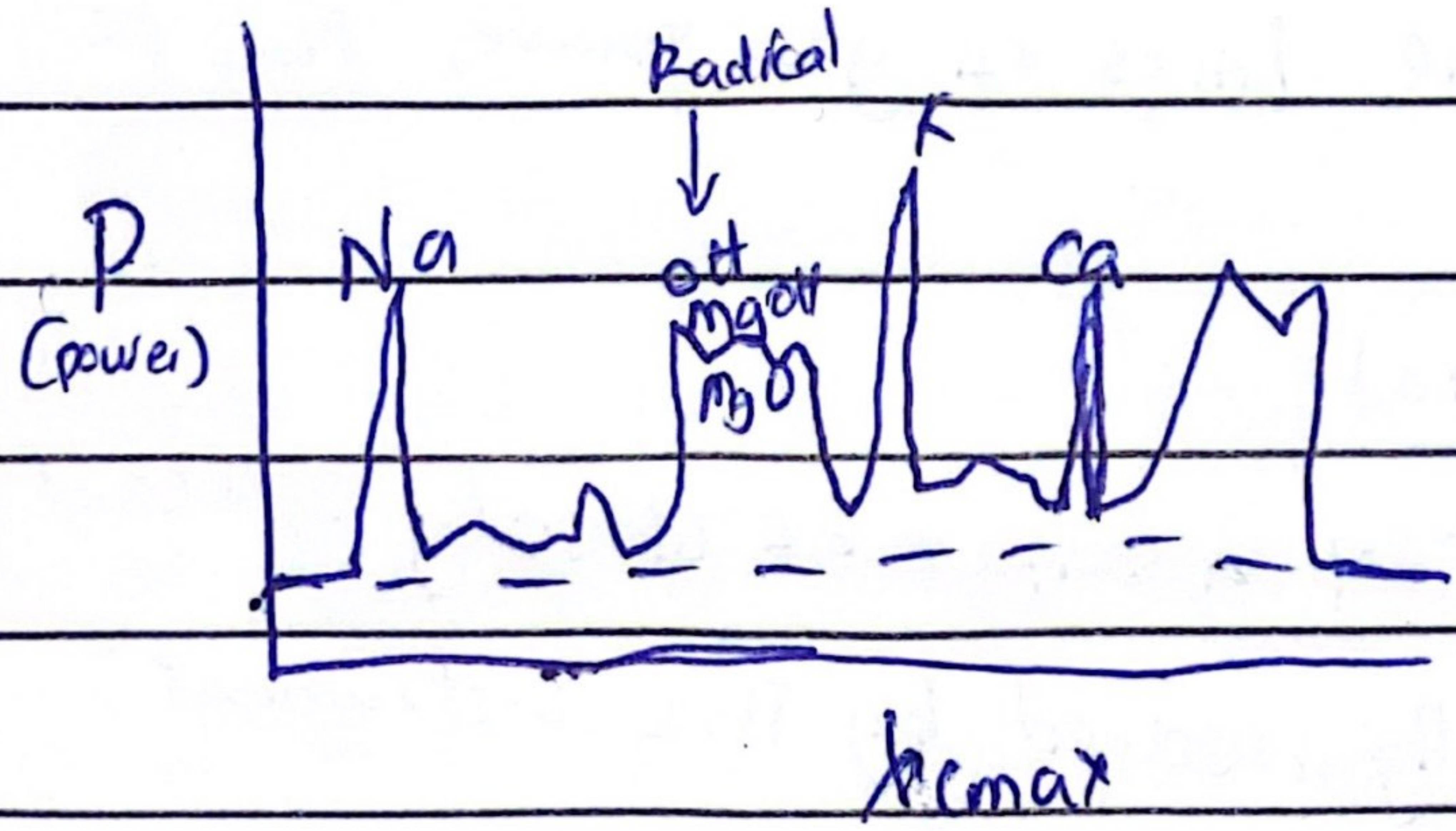
(1) bombardment with electrons or other elementary particles which generally leads to the emission X- radiations,

(2) Exposure to an electric current and AC spark or an intense heat source (flame, DC Arc or furnace) Producing UV, visible or IR radiation.

(3) The radiation with a beam of electromagnetic radiation which produces flourescence radiation;

(4) An exothermic chemical reaction that produces Chemiluminscence. Radiation from an excited sorce is conveniently characterized by means of an emission spectrum which is a plot of the relative power of the emitted radiation as a function of wavelength or frequency. ~~or frequency~~

Diagram of a typical emission spectrum



The emission spectrum above was obtained by aspirating a brime solution in to an oxy hydrogen flame, which produced three types of spectral namely:

(i) lines (ii) Bands (iii) Continuum

Line spectrum

Line spectral in the UV and visible regions are produced when the radiating species are individual atomic particles that are well seperated in a gas phase

The individual particle of a gas behave independently of one another and the spectrum consist of series of sharp lines with width of 10^{-5} nm (10^{-4} Å)

In the diagram above, lines of gas phase, Na, K, Ca are identified

Band Spectral

Band spectral consist of a series of closely spaced lines that are not fully resolved by the instrument used to obtain the spectrum

Bands arise from the numerous quantized level that are superimposed on the ground state electronic energy level of small molecules or gaseous radicals such OH, MgOH

Continum Spectral

A continum radiation produced when solid are heated to incandescence. Thermal radiation of this kind which is called black body radiation is characteristic of the emitting surface rather than the material of which that surface is composed.

General Designs of Optical Instruments

Instruments used for the UV, visible and IR have enough features in common that they are often reffered to as optical instrument even though the human eye is not visible to IR wavelength. Optical spectroscopy method are based on phenomenon as listed below:

(1) Absorption

(2) Fluorescence

(3) Phosphorescence

(4) scattering

(5) emission

(6) Chemiluminescence.

Although, the instrument for measuring each differ in configuration, most of their basic components are remarkably similar. Also, the required properties of these components are the same regardless of whether they apply to UV, visible or IR portion of the component

Typical spectroscopy instrument contain the following 5 components

(1) Stable source of radiant energy

(2) Transparent container for holding ~~containing~~ the sample (Curvette) made of quartz.

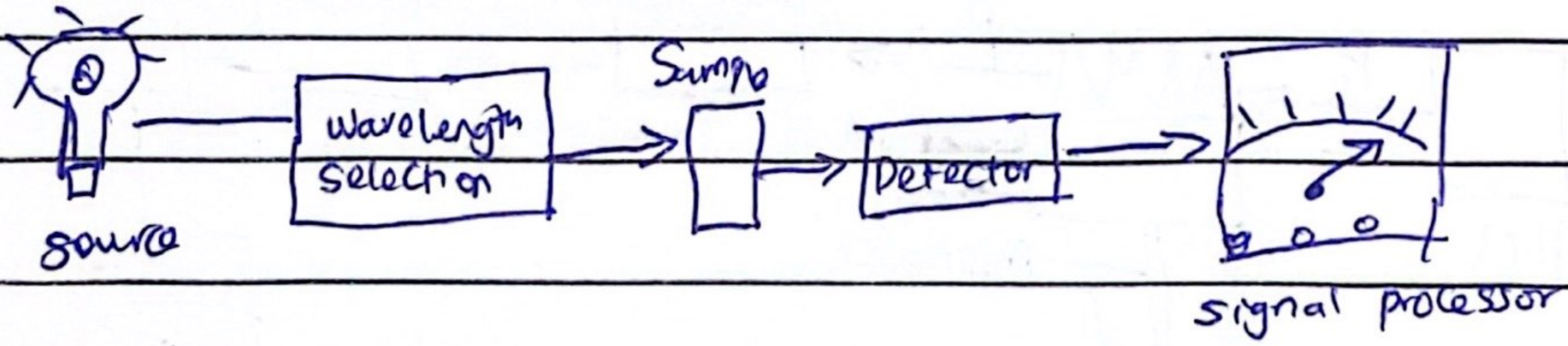
(3) Device that isolates the restricted region of the spectrum for measurement

(4) Radiation detector which converts radiant energy

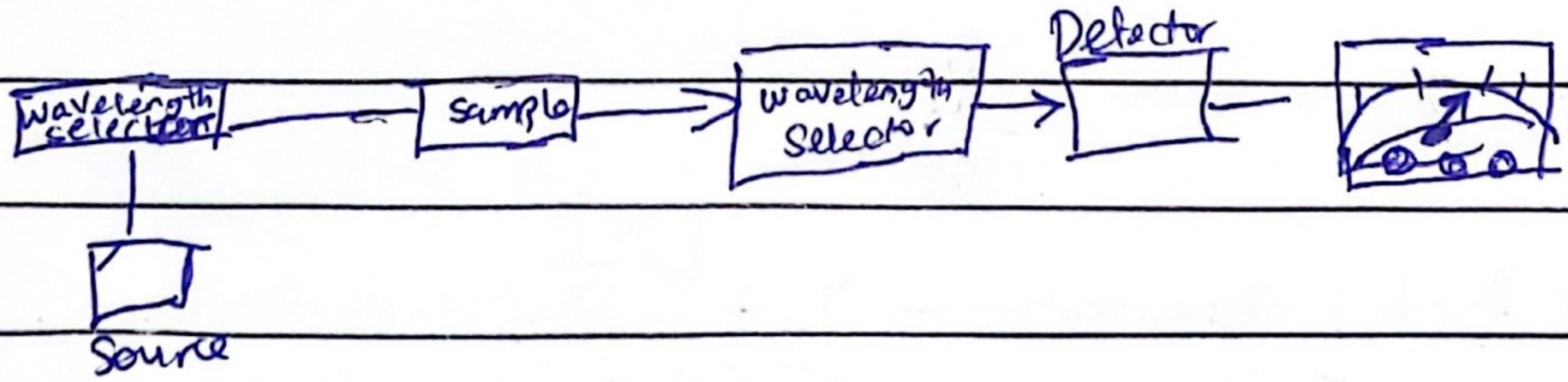
to usabe electrical signal

(3) Signal processor and read out which displace the transduce signal on a meter scale or a computer stream or a digital screen or another recording metal.

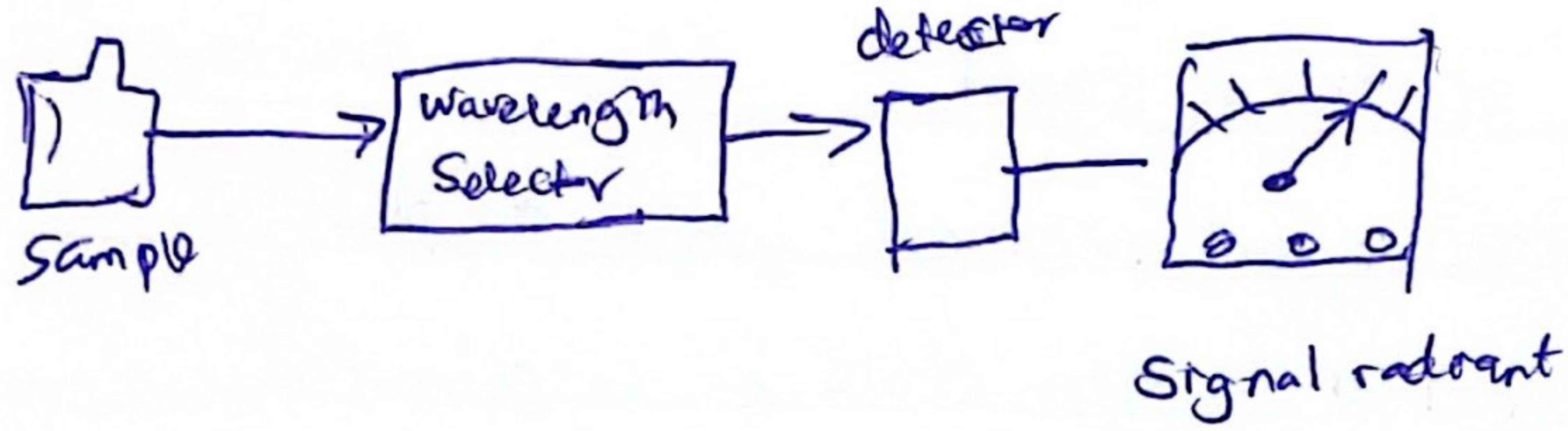
(a) Absorption Measurement



(b) Fluorescence



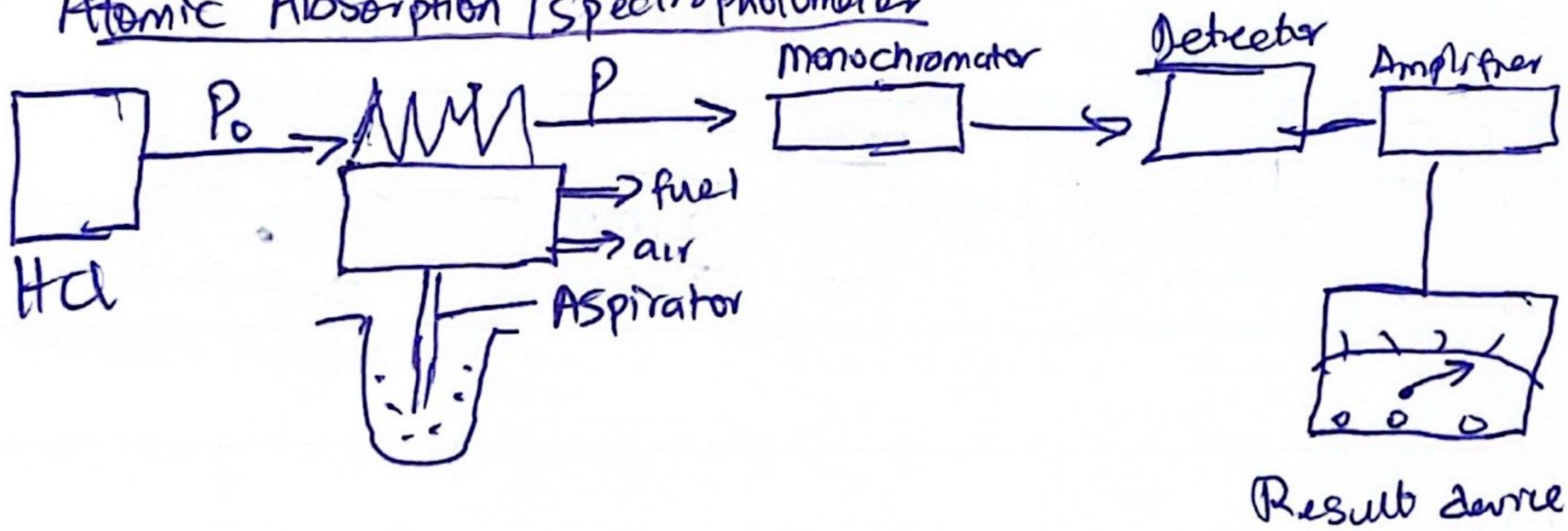
(9) Emission spectrum



The source, detector, signal processor are arranged in the same position. I.e most component are Similar.

It is the arrangement that is different.

Atomic Absorption / spectrophotometer



* Dilution factor $= \frac{V_f}{m_i}$

* Actual concentration $[M]_a$ = $\frac{\text{Instrumental concentration } [M]_i}{\text{~~Dilution factor~~}}$ × dilution factor

Example

$[M]_i = 2.85\ \mu g/g$ 0.25g soil → 50ml

$d.f = \frac{50}{0.25} = 200$

$[M]_a = [M]_i \times d.f$

$= 2.55 \times 200$

Interferences

Two types of interference, these are

(i) Spectral interference (ii) Chemical interferences

Spectral Interference: presence

* To cut of interference, we purify

Chemical: stable compound formation

Molecular absorption: has very high temperature

* State five chemical interferences that can occur in ADS, discuss any 2 of them.

* How do we overcome chemical interferences?

(i) use of a releasing agent (ii) extraction of

(iii) add excess of ionizing supressant