Photochemistry

Photophysics and photochemistry both deal with the impact of energy in the form ofphotons on materials. Photochemistry focuses on the chemistry involved as a material isimpacted by photons while photophysics deals with physical changes that result from theimpact of photons. We will focus on some of the basic principles related tophotophysics and photochemistry followed by general examples. Finally these principleswill be related to photosynthesis. In many ways there is a great similarity between amaterial's behavior when struck by photons, whether the material is small ormacromolecular. Differences are related to size and the ability of polymers to transferthe effects of radiation from one site to another within the chain or macromolecularcomplex.

Photophysics and Photochemistry

Photophysics involves the absorption, transfer, movement, and emission of electromagnetic, light, energy without chemical reactions. By comparison, ***photochemistry*** involves the interaction of electromagnetic energy that results in chemical reactions.

Light Absorption

Light is composed of particles known as photons, each of which has the energy ofPlanck's quantum, hc/λ; where h is Plank's constant, c is velocity of light and λ is thewavelength of the radiation. Light has dualistic properties of both waves and particles; ejection of electrons from an atom as a result of light bombardment is due to the particle behavior while the observed light diffraction at gratings is attributed to the wave properties.

The Grotthus-Draper law states that photophysical/photochemical reactions only occur when a photon of light is absorbed. This forms the basis for the First Law ofPhotochemistry, that is, only light that is absorbed can have aPhotophysical/photochemical effect.

We can write this as follows.

$$M + light \longrightarrow M^*$$

Here M^* is M after it has taken on some light energy that it has acquired energy duringa photochemical reaction. The asterisk is used to show that M is now in an excited state.

Optical transmittance, T, is a measure of how much light that enters a sample is absorbed.

$$T = I/I_o$$

If no light is absorbed then $I = I_o$. Low transmittance values indicate that lots ofthe light has been absorbed.

Most spectrophotometers give their results in optical absorbency, A, or opticaldensity (same) which is defined as: $A = \log (I/I_o)$ so that $A = \log (1/T) = -\log T$

Transmittance $T = \frac{I}{I_0}$

Percent Transmittance $\%T = \frac{I}{I_0} \times 100\%$

Absorbance $A = -\log T$

$= -\log \frac{I}{I_0}$

$= \log \frac{I_0}{I}$

Beer's law states that A, the absorbance of chromophores, increases in proportionto the concentration of the chromophores where k is a constant.

$$A = k\,c$$

Beer's law predicts a straight line relationship between absorbance andconcentration and is often used to determine the concentration of an unknown afterconstruction of the known absorbance verses concentration line.

The optical path, l, is the distance the light travels through the sample. This isseen in looking at the color in a swimming pool where the water is deeper colored at the deep end because the optical path is greater. This is expressed by Lambert's law wherek' is another empirical constant.

$$A = k'\,l$$

To the eye some colors appear similar but may differ in intensity when c and l arethe same. These solutions have a larger molar absorption coefficient, ε, meaning theyadsorb more. The larger the adsorption coefficient the more the material adsorbs.

The Beer-Lambert law combines the two laws giving

Classification of Analytical Methods

Qualitative instrumental analysis is that measured property indicates *presence* of analyte in matrix

Quantitative instrumental analysis is that magnitude of measured property is proportional to *concentration* of analyte in matrix

Species of interest: All constituents including analyte and Matrix-analyte (concomitants)

Often need pretreatment - chemical extraction, distillation, separation, precipitation

(A) Classical:

Qualitative - identification by color, indicators, boiling points, odors

Quantitative - mass or volume (e.g. gravimetric, volumetric)

(B) Instrumental

Qualitative - chromatography, electrophoresis and identification by measuring physical property (e.g. spectroscopy, electrode potential)

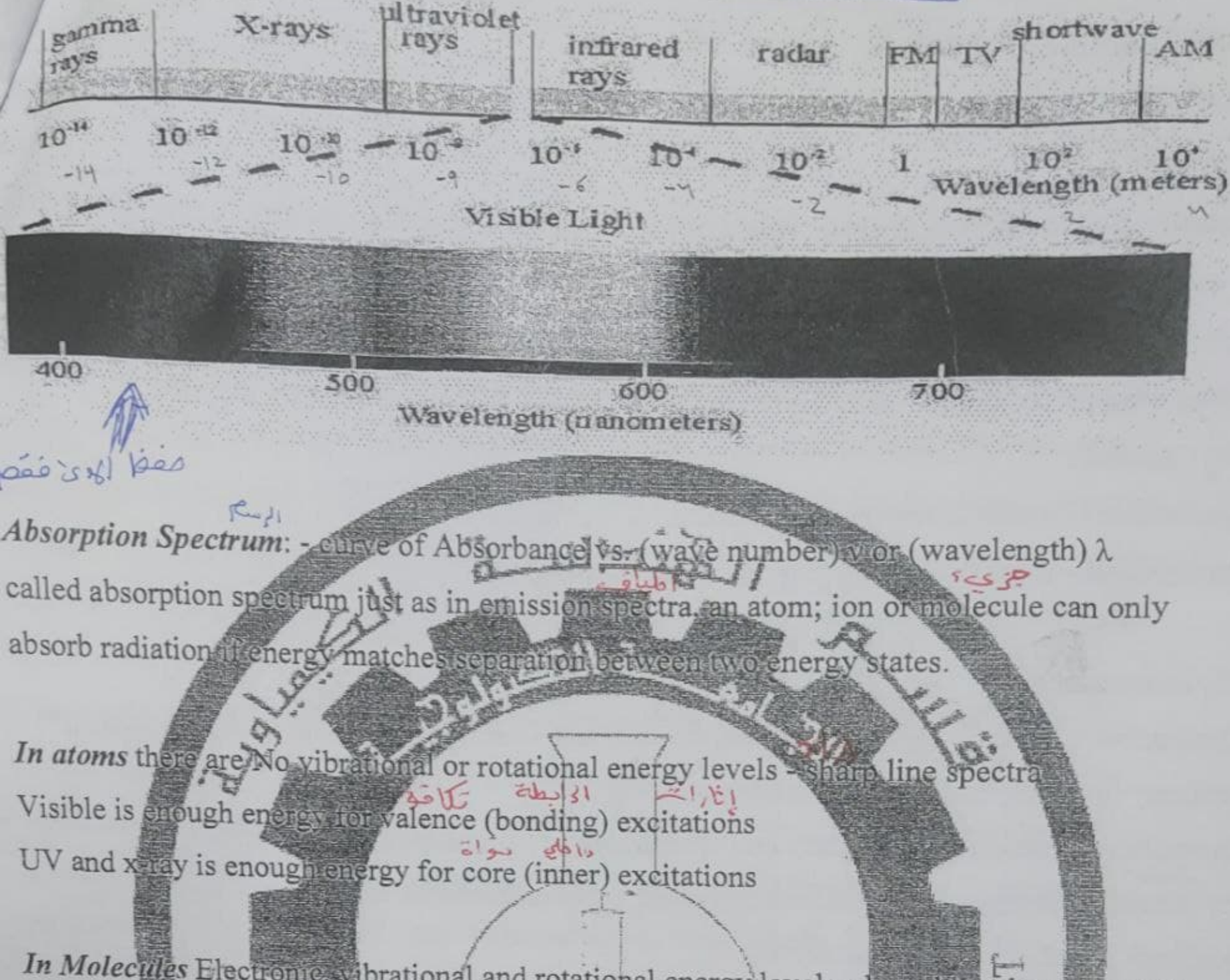
Quantitative - measuring property and determining relationship to concentration (e.g. spectrophotometry, mass spectrometry) often, same instrumental method used for qualitative and quantitative analysis

Instrumental Analysis:-

Instrument are widely used to measure some properties which are directly related to the concentration of the sample to be analyzed, the instrument is some time used rather than indicator to locate the end point of titration such as potentiometric titrations

Spectrochemical techniques

Is one of the optical methods widely used for analysis, it is based on the measurement of the wavelength frequency or energy of electromagnetic radiation (EMR) that either absorbed or emitted by the sample the EMR spectrometry is divided into several energy regions as shown :-



Absorption Spectrum: - curve of Absorbance vs. (wave number) ν or (wavelength) λ called absorption spectrum just as in emission spectra, an atom; ion or molecule can only absorb radiation if energy matches separation between two energy states.

In atoms there are No vibrational or rotational energy levels - sharp line spectra

Visible is enough energy for valence (bonding) excitations

UV and x-ray is enough energy for core (inner) excitations

In Molecules Electronic, vibrational and rotational energy levels - broad band spectra with many features

$\Delta E = \Delta E$ electronic + ΔE vibrational + ΔE rotational

For each electronic state - many vibrational states

For each vibrational state - many rotational states

Absorption spectra affected by

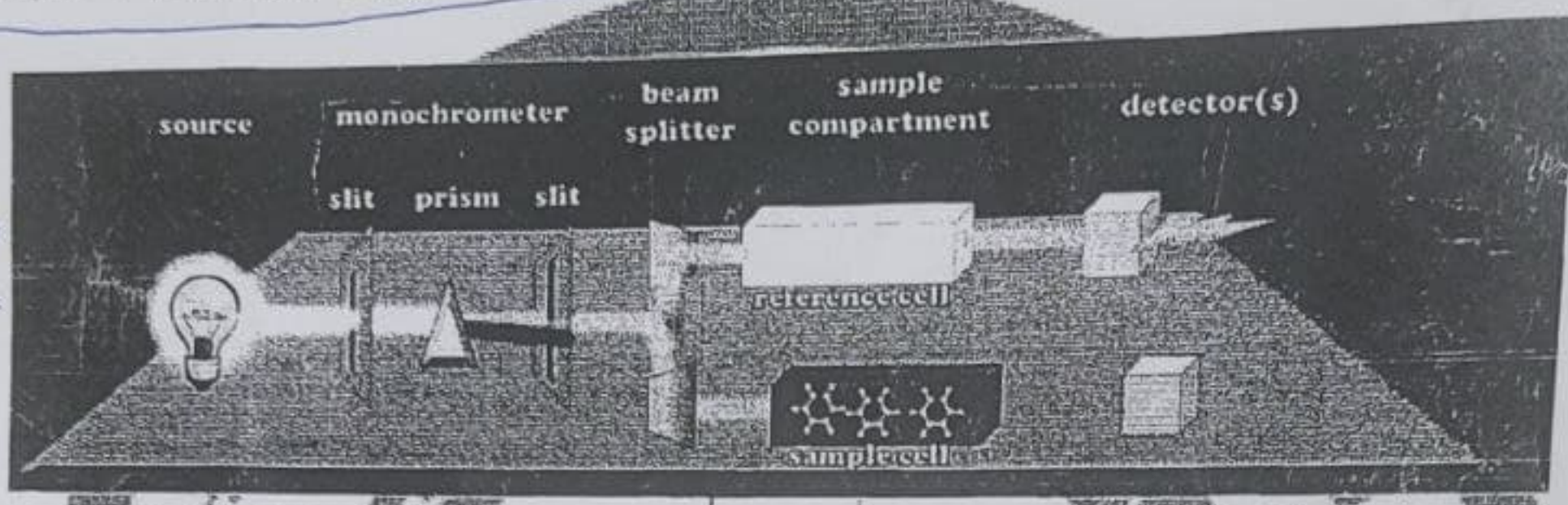
(1) Number of atoms in molecule more features

(2) Solvent molecules blurred features

UV,Ultraviolet spectrometry

when two atoms share to make new bond; there are electron in both atom will participate to form this bond the electrons occupied new orbital called molecular bonding orbital with low energy and antibonding orbital with high energy and the electron how don't share called nonbonding.

When the molecular absorb energy in UV range; electronic transfer will happened (σ-σ^*, σ-π^*, π-π^*, n- σ^*, n- π^*, π-σ^*) (200-380nm)



Infrared Spectroscopy(IR)

- IR is used both together information about the structure of a compound and as an analytical tool to assess the purity of a compound.
- Frequency, ν, is the number of wave cycles that pass through a point in one second.
- It is measured in Hz, where 1 Hz = 1 cycle/sec. ***Wavelength***, λ (lambda), is the length of one complete wave cycle. It is often measured in cm (centimeters). Wavelength and frequency are inversely related:

$$\nu = \frac{c}{\lambda} \text{ and } \lambda = \frac{c}{\nu}$$

Where: c is the speed of light, 3×10^{10} cm/sec

- Energy is related to wavelength and frequency by the following formulas:

$$E = h\nu = \frac{hc}{\lambda}$$

Where: h = Planck's constant, 6.6×10^{-34} joules-sec

- Note that energy is directly proportional to frequency and inversely proportional to wavelength.

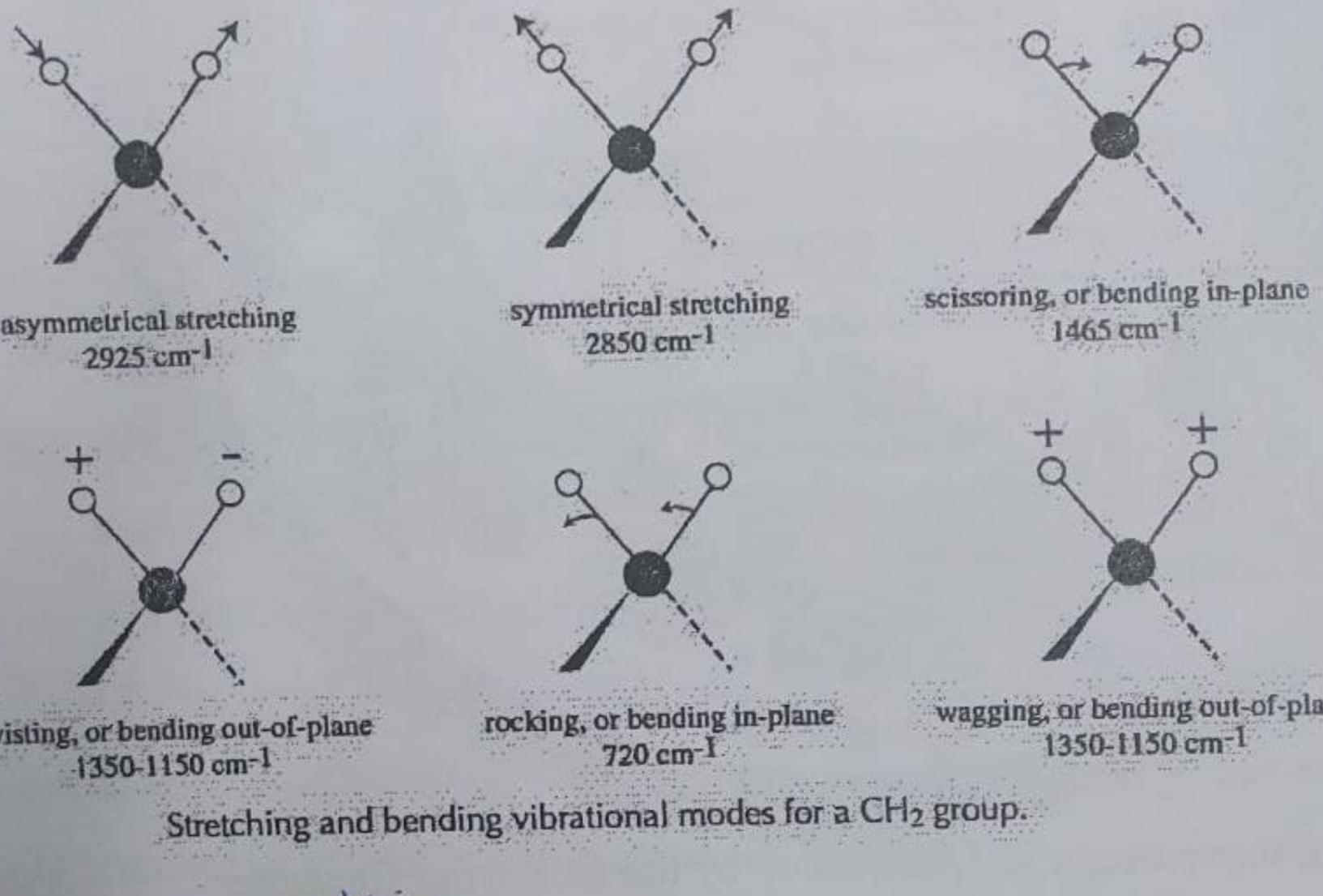
- IR is a device that measures the intensity of the electromagnetic spectrum which is between the visible and Microwave (400-4000 cm^{-1})and expressed either transmittance or absorption: $A = \log(1/T)$

n increase in wavenumber corresponds to an increase in energy, when the molecule bsorb the energy will start to vibrate; stretching (changing the length of the bond or ending changing the angle of the bond)

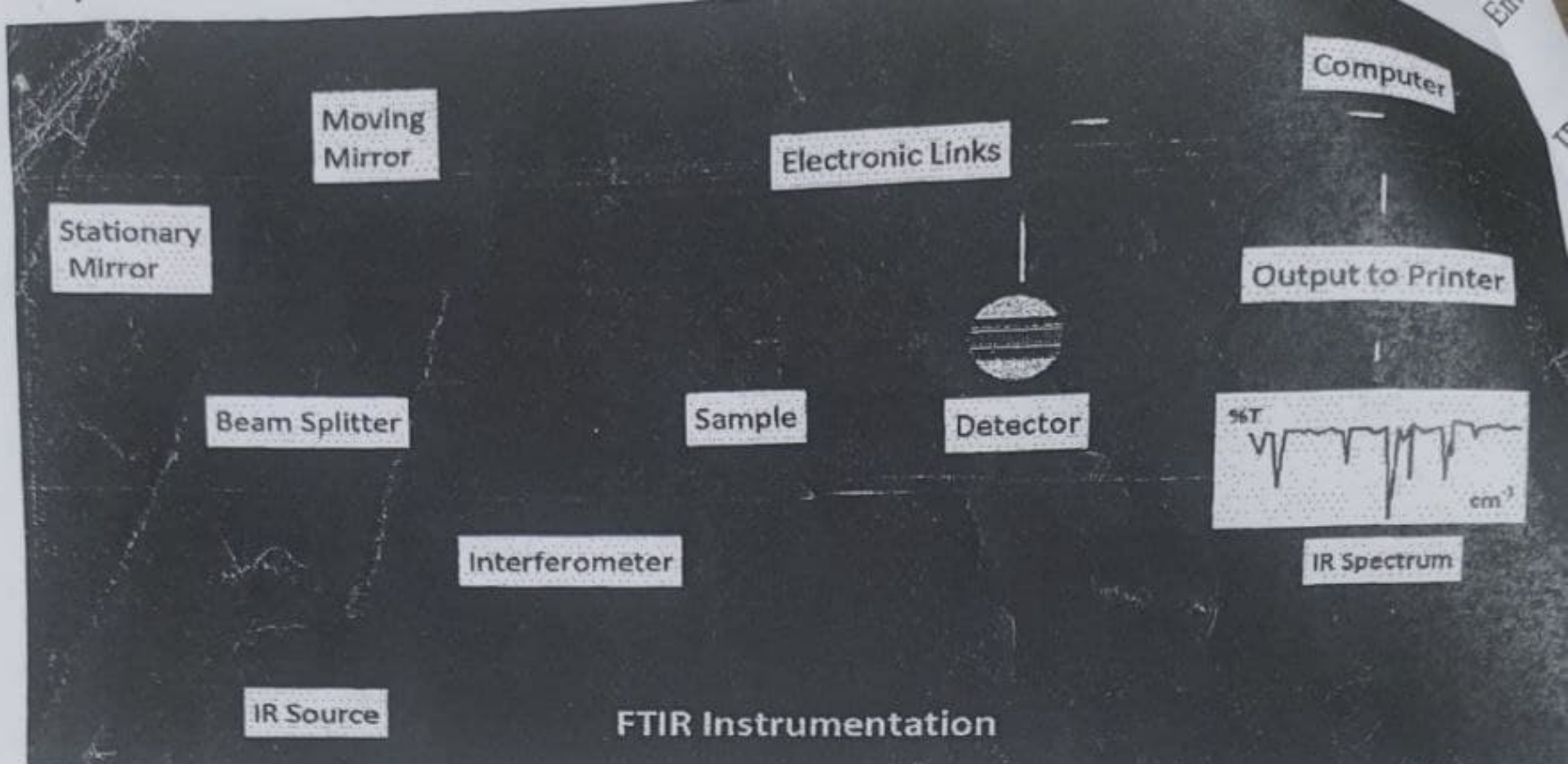
- we can calculate the frequency of bond from Hooke law

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \qquad \mu = \frac{M1*M2}{M1+M2}$$

- K= $5*10^5$ dyne/cm for single bond, $10*10^5$ dyne/cm for double bond, $15*10^5$ dyne/cm for treble bond
- C = is the velocity of light =3×10^{10} cm/sec.



Stretching and bending vibrational modes for a CH_2 group.

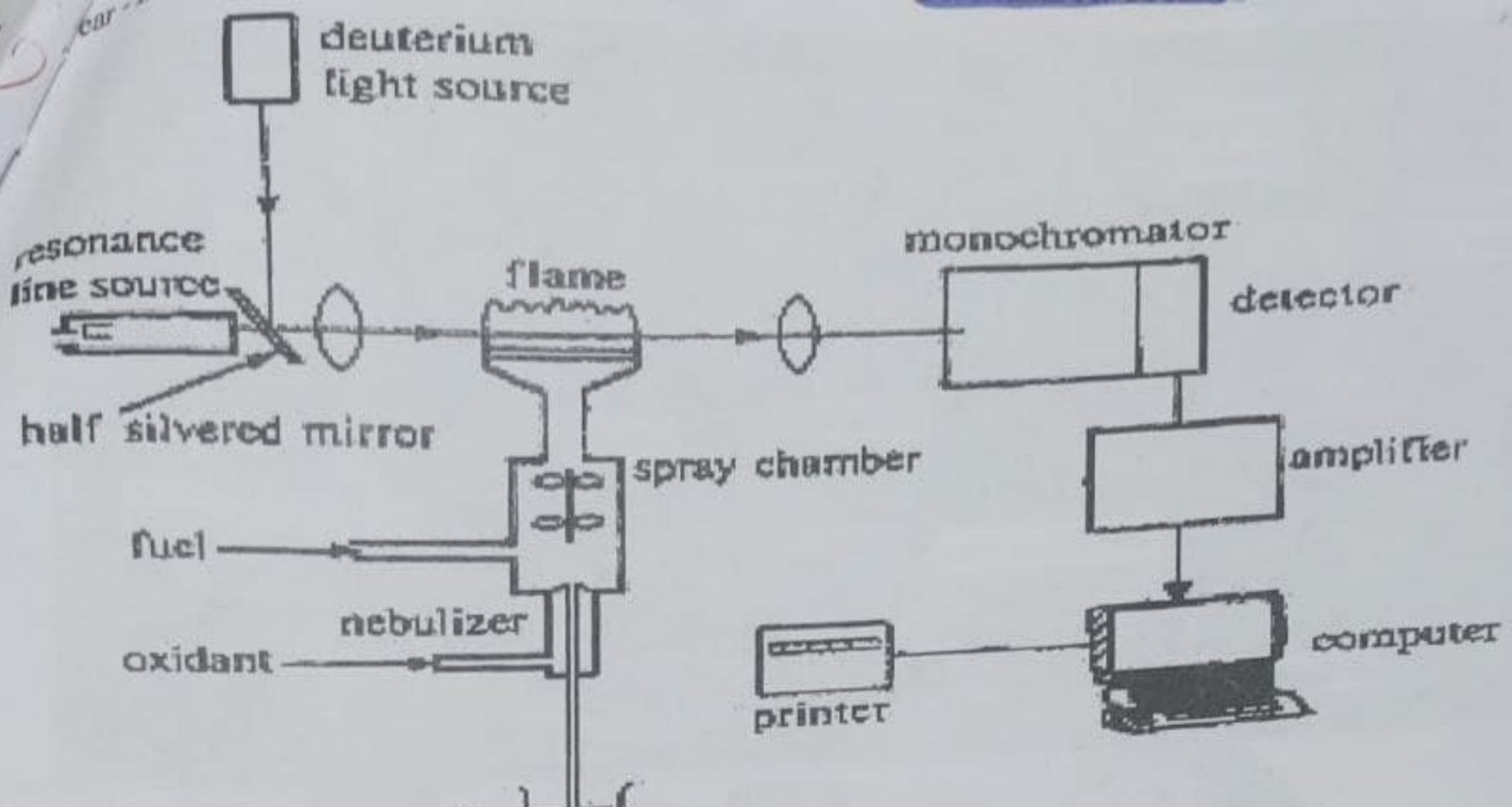


Atomic absorption spectrometry: AAS

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of metals. It is so sensitive that it can measure down to ppb (µg/L) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. The method is based on the absorption of radiation by free atoms

While a sample is being aspirated into a flame, a light-beam is directed through the flame into a monochromator and onto a detector that measures the amount of light absorbed by the atomised element in the flame. A source lamp composed of the element of interest is used because each element has its own characteristic wavelength. This makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range. Most atomic absorption instruments are also equipped for operation in an emission mode

Atomic absorption spectrophotometer consisting of a light source emitting the line spectrum of an element, a device for vaporising the sample, a means of isolating an absorption line and a photoelectric detector with its associated electronic amplifying and measuring equipment



Chromatography

Is a method of analysis based on separation of sample components by distribution them between a stationary and mobile phases. In general, such separation depends on the relative attraction of each component to the two phases. The substance which is more strongly attracting to the mobile phase than to the stationary phase is moved along with the mobile phase more rapidly than another substance which is more strongly attracted to the stationary phase.

Chromatography is classified into different categories depending on the physical state of the stationary and mobile phases as follows

Type of chromatograph	mobile phase	stationary phase
Gas -liquid	gas	liquid
Gas -solid	gas	solid
Liquid-liquid	liquid	liquid
Gel-permeation	liquid	Gel

Retentiontime T_R : is The time required for the mobile Phase to remove The component from The stationary Phase.

pH-meter

A pH Meter is a device used for potentiometrically (voltmeter which is calibrated to convert voltage to pH units) measuring the pH, which is either the concentration or the activity of hydrogen ions, of an aqueous solution. It usually has a glass electrode plus a calomel reference electrode, or a combination electrode. pH meters are usually used to measure the pH of liquids, though special probes are sometimes used to measure the pH of semi-solid substances.

The electrode that does the most important job, which is called the glass electrode, has a silver-based electrical wire suspended in a solution of potassium chloride, contained inside a thin bulb (or membrane) made from a special glass containing metal salts (typically compounds of sodium and calcium). The other electrode is called the reference electrode and has a potassium chloride wire suspended in a solution of potassium chloride. The potassium chloride inside the glass electrode is a neutral solution with a pH of 7, so it contains a certain amount of hydrogen ions (H+). Suppose the unknown solution you're testing is much more acidic, so it contains a lot more hydrogen ions. What the glass electrode does is to measure the difference in pH between the two solutions by measuring the difference in the voltages their hydrogen ions produce. Since we know the pH of the potassium chloride solution (7), we can figure out the pH of the unknown solution.

When you dip the two electrodes into the unknown test solution, some of the hydrogen ions move toward the outer surface of the glass electrode and replace some of the metal ions inside it, while some of the metal ions move from the glass electrode into the unknown solution. This ion-swapping process is called ion exchange, and it's the key to how a glass electrode works. Ion-swapping also takes place on the inside surface of the glass electrode from the potassium chloride solution. The two solutions on either side of the glass have different acidity, so a different amount of ion-swapping takes place on the two sides of the glass. This creates a different degree of hydrogen-ion activity on the two surfaces of the glass, which means a different amount of electrical charge builds up on them. This charge difference means a tiny voltage (sometimes called a potential difference, typically a few tens or hundreds of millivolts) appears between the two sides of

الكيمياء الضوئية Photochemistry

تتفاعل الكيمياء الضوئية والفيزياء الضوئية مع الطاقة (بصيغة فوتونات) وتأثيرها على المواد ...

الكيمياء الضوئية تركز على الكيمياء (التي تتضمن مادة وتم وصفها بالفوتونات

في حين الفيزياء الضوئية تتعامل مع التيارات الفيزيائية الناتجة من

الفيزياء الضوئية تتضمن: الامتصاص absorbtion ، الانتقال transfere

الحركة والانبعاث الكهرومغناطيسي والطاقة :- بمعنى اي تفاعل كيميائي

في حين photochemistry تتخذ من الطاقة الكهرومغناطيسية

كناتج من التفاعل الكيميائي ..

Light absorption

quantum ← الطاقة الكم ← photons الضوء يتكون من مجموعة من

فوتون ← طاقة بزمك (الكم)

hc/λ ← h ثابت بلانك
c ← سرعة الضوء
λ ← الطول الموجي للإشعاع

$M + light \xrightarrow{\text{تتحول الى}} M^*$

M ← ذرة مستقرة stable
light ← تكتسب طاقة
M^* ← ذرة مهيجة excited

Photo chemical Reaction ← يدخل في تفاعل ← تفاعل كيميائي

optical Transmittance

كنفاذية ضوئية أو البصرية

$T = I / I_0$

كمية الضوء الخارج من النموذج بعد دخول الضوء له

I ← شدة الضوء الخارج
I_0 ← شدة الضوء النافذ

إذا لم يتم امتصاص الضوء $I = I_0$

Absorbance

A ← الامتصاصية

$A = -\log T \Rightarrow -\log \frac{I}{I_0} \Rightarrow A = \log \frac{I_0}{I}$

$\log$ ← قانون الامتصاص

قانون Beer ← A ← c ← K ثابت

فإن الامتصاصية تزداد اوتناسب طردياً مع التركيز

$A = K \cdot C$

* حال معرفة قيمة A بالتجربة على الخط المستقيم يمكن معرفة تركيز المادة المجهولة:

A تتناسب طردياً مع التركيز

Classification of Analytical Methods

نقسم الطرق التحليلية وكما ذكرنا سابقاً الى صنفين

Quantitative ← → Qualitative

Quantitative
كلي
تحليل آلي يقدر كمية الصفات التي تتشابه مع تركيز المادة المحللة

Qualitative
نوعي
تحليل آلي Instrument
تدرس او تقيس الصفات
التي تميز نوعية او وجود المركب

تحضير العينة: يجب تحضير العينة بسبب عدة طرق مثل extraction استخلاص
تقطير -- distillation الفصل -- Seperation الترسيب
Precipitation.

كطرق كلاسيكية Classic
Qualitative :- يمكن تشخيصها عن طريق اللون، دلائل Indicator
B.P درجة الغليان و الرائحة odor
Quantitative :- كتلة أو الحجم (وزنية، حجمية)

الطرق الآلية: Instrumental
Qualitative نوعية: كروموتوغرافي - chromotography
Quantitative :- قياس الخواص وأكتساب المعلومات الرياضية مع التركيز (الطيفية - طيف الكتلة mass spectrometry)
طرق شائعة للقياس والتقدير النوعي -

Instrumental Analysis التحليل الآلي:-

تستعمل بشكل واسع لقياس بعض الصفات التي لها علاقة بتركيز المكون في النموذج المراد تحليله

Spectrochemical techniques طيفيات كيميائية

أحد الطرق البصرية المستخدمة بشكل واسع للتحليل والتي تعتمد على قياس تردد الطول الموجي Wavelength frequency أو قياس طاقة إشعاع الكهرومغناطيسي (EMR) ←

Electro magnetic Radiation

كل إشعاع أو المنبعث من النموذج

EMR يمكن تقسيمه الى بضع مناطق الطاقة energy regions

كما سيرد في المحاضرة

كما تستخدم في تحليل كل إشعاع له مستوى طاقي معين

gama rays	اشعة غاما	كل إشعاع يعمل ضمن طول موجي معين وحسب ما مبين في المحاضرة
x-ray	اشعة x السينية	
Ultra violet	U.V فوق البنفسجي	
Infra red	تحت الحمراء IR	
radar	اشعة الرادار	
FM		
TV		
Short wave		

واخيراً A.M

طيف الامتصاص Absorption Spectrum

هو الحني الموضح بين الامتصاصية Absorbance عند الطول الموجي λ أو wave number

الذرة والايون والجزيئة يمتلكون امتصاص طاقة إشعاع وهو شابه للطيف في الذرة atom ليس هناك مستوى طاقي دوراني او اهتزازي

طيف خطي حاد Sharp line spectra

في الجزيئة Inmolecule مستويات طاقية دورانية واهتزازية والكترونية

$$\Delta E = \Delta E_{\text{electronic}} + \Delta E_{\text{Vibration}} + \Delta E_{\text{rotation}}$$

الكتروني اهتزازي دوراني

يتأثر طيف الامتصاص بالعوامل التالية

1- No. of atoms in molecule
عدد الذرات في الجزيئة (تأثيرها واضح)

2- Solvent molecule
مذيبات، مذيب (تأثيرها غير واضح) (اقل) تأثيراً

قمنا فوق البنفسجية Ulth violet U.V

عندما تشارك ذرتان لعمل آصرة جديدة هناك الكترونات لا كل ذرة ستشارك لتكوين تلك الاصرة سوف تحتل هذه الالكترونات اوربتالات جديدة تسمى (اوربتالات الترابط الجزيئي) ذات الطاقة الواطئة

و (اوربتالات غير ترابطية) antibonding orbital ذات طاقة عالية

والالكترونات الغير مشتركة بالترابط تسمى nonbonding

عندما تمتص الجزيئة الطاقة (طاقة فوق البنفسجية) ستحدث انتقالات الكترونية Electronic transfer

سكما $\sigma \rightarrow \sigma^*$

$\sigma \rightarrow \pi^*$

باي $\pi \rightarrow \pi^*$

$n \rightarrow \pi^*$

$\pi \rightarrow \sigma^*$

مثلا

ضمن المدى (200-380)

nm ⟶ nano meter

نانومتر هي وحدة قياس الطول الموجي

ذو المدى الذي تكون فيه أشعة U.V هو بين (200-380) nm

Infra red spectroscopy (IR)

طيفية تحت الحمراء

١. تستخدم طريقة طيفية I.R لغرضين

I Structure ٩/ تعطي معلومات لحزمة البناء او الصيغة للمركبات

Purity of compound b/ انها اداة (tool) لحزمة نقاوة المركبات

* أدنى الذي تكون فيه I.R هو $(400-4000)\ cm^{-1}$

*2 التردد frequency ν : عدد دورة الموجة No. Wave cycle

التي تمر خلال نقطة ؟ كانت واحدة

*3 يقاس التردد بـ HZ هرتز (وحدة قياس التردد)

HZ = 1 cycle/sec

يتناسب التردد والطول الموجي تناسباً عكسياً

Inversly Proportion

$\nu = \frac{c}{\lambda}$ ← التردد — سرعة الضوء ← c

λ ← الطول الموجي

*4 العلاقة بين الطاقة والطول الموجي والتردد

$E = h\nu \Rightarrow E = \frac{hc}{\lambda}$ ← طاقة

h هو ثابت بلانك = 6.6×10^{-34} J/Sec

*5 الطاقة تتناسب طردياً مع التردد direct Proportion

وعكسياً مع الطول الموجي Inversely //

Atomic Absorption Spectrum (AAS)
طيف إمتصاص ذري

Instrumental Analysis

وهي تقنية وتقنيات تحليل آلي والتي يتم عن طريقها قياس تركيز العناصر

وتعتبر طريقة حساسة جداً قد تصل الى تركيز النموذج (µg/L) ملليكرو جرام لكل لتر

هذه الطريقة تعتمد على امتصاص الاشعاع من الذرات الحرة.

[ميكانيكية عمل الجهاز غير مطلوبة] فقط اجزاء الجهاز

وطيف الامتصاص الذري يشتمل على

Line spectrum الطيف الخطي للعنصر

1. مصدر ضوء light source يبعث
2. جهاز لتبخير أو تذرية النموذج Vaporising the Sample
3. منطقة عزل الخط المتص isolating Part
4. كاشف الطيف الكتروني Photoelectric detector
5. جهاز تضخيم amplifyer
6. اداة قياس measurry equipment

ملحوظة اجزاء الجهاز للتوضيح فقط
ليس للحفظ

chromatography
إطيافية اللونية

وهي اصل الطرق التحليلية التي تعتمد على فصل separate
مكونات الموقع عن طريق توزيعها (distribution)
بين طورين two Phases [mobile + Stationary]
طور متحرك طور ثابت

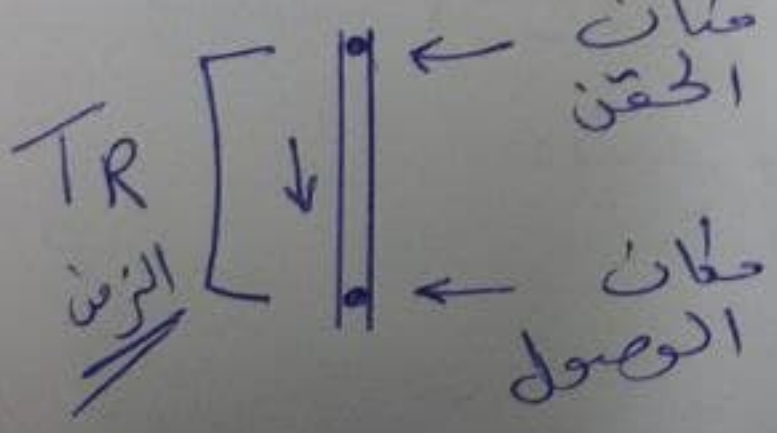
هذا الفصل يعتمد على مدى انجذاب مكونات النموذج لكل طور
فهناك مواد تنجذب الى الطور الثابت بسرعة وهناك اخرى تنجذب الى
الطور المتحرك بسرعة.

تصنف طريقة chromatography الى عدة اصناف تبعاً للحالة الفيزيائية
لكلا الطورين الثابت والمتحرك [حيث يوجد ثلاث حالات للمواد]

T_R Retention time أو زمن الاحتجاز

يمكن حسابه من المخطط وهو الزمن المحسوب منذ حقن النموذج
وحتى الوصول الى القمة أو الوقت الذي تستغرقه المادة المحقونة
داخل عمود الكروموتوغرافي لكي تصل الى الطرف الاخر للعمود
والظهور على الكاشف

Injection



PH-meter

قياس الدالة الحامضية

هو جهاز يستخدم لقياس فرق الجهد Potentiometer

(الفولتية التي تتحول الى قيمة PH)

ويُستفاد منها لقياس التركيز أو قياس فعالية ايون الهيدروجين للمحاليل المائية aqueous Soln.

* يجب احتواء pH meter على قطب زجاجي glass electrode

و قطب مرجع Calomel reference electrode

أو قطب مقد Combine electrode

* عادةً يستخدم pH meter لقياس pH للسوائل وللمواد شبه صلبة Semi-Solid

(كالعجوينة)