Srinivasan College of Arts and Science

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DEPARTMENT OF CHEMISTRY

Course Material for B. Sc., Chemistry Students

Physical Chemistry II

Subject Code : 16SCCCH9

Prepared & Developed

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1. Explain the Ostwald's dilution law.

According to Arrhenius theory of electrolyte dissociation, the molecules
Of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by Ostwald that like chemical equilibrium, law of mass action van be applied to such systems also.
Consider a binary electrolyte AB which dissociates to A^+ and B^- ions and the equilibrium state is represented by the equation:

$$AB \leftrightarrow A^+ + B^-$$

Initially t = o

C 0 0

At equilibrium

$$C(1\ \ \alpha)\ C\alpha\ C\alpha$$

So, dissociation constant may be given as

$$K = [A^+][B^-]/[AB] = (C\alpha * C\alpha)/C(1 - \alpha) = C\alpha^2 (1 - \alpha) \text{ .... (i)}$$

For very weak electrolytes,

$$\alpha <<< 1, (1 - \alpha) = 1$$

$$\therefore$$

$$K = C\alpha^2$$

$$\alpha = \sqrt{}K/C\text{....... (ii)}$$

Concentration of an y ion = $C\alpha = \sqrt{CK}$.

From equation (ii) it is a clear that degree of ionization increases on dilution.
Thus, degree of dissociation of a weak electrolyte is proportional to the square root of dilution.
Limitations of Ostwald's dilution law:
The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of 'α' is determined by conductivity measurements by applying the formula Λ/Λ_∞. The value of 'α' determined at various dilutions of an electrolyte when substituted in Eq. (i) gives a constant value of K only in the case of weak electrolytes like CH_3COOH, NH_4OH, etc. the cause of failure of Ostwald's dilution law in the case of strong electrolytes is due to the following factors"

(i)The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilutions and $\Lambda/\Lambda\infty$ does not give accurate value of 'α'.
(ii) When conce ntration of the ions is very high, the presence of charges on the ions
Appreciably effects the equilibrium. Hence, law of mass action its simple form cannot be strictly applied in the case of string electrolytes.

2.Discuss the Arrhenius theory of strong electrolyte (1) Postulates of Arrhenius theory

(i) In aqueous solution, the molecules of an electrolyte undergo spontaneous dissociation to form positive and negative ions.

(ii) Degree of ionization (α)

= Number of dissociate d molecules / Total number of molecules of electrolyte before dissociation

(iii) At moderate concentrations, there exists an equilibrium between the ions and undissociated molecules, such as, $NaOH \rightarrow Na^+ + OH^-$; $KCl \rightarrow K^+ + Cl^-$

This equilibrium state is called ionic equilibrium.

(iv) Each ion behaves osmotically as a molecule.

(2) Factors affecting degree of ionization

(i) At normal dilution, value of α is nearly 1 for strong electrolytes, while it is very less than 1 for weak electrolytes.

(ii) Higher the dielectric constant of a solvent more is its ionising power. Water is the most powerful ionising solvent as its dielectric constant is highest.

(iii) $\alpha \propto$ 1/Con. of solution $\propto$ 1/wt.of solution

$\propto$ Dilution of solution $\propto$ Amount of solvent

(iv) Degree of ionisation of an electrolyte in solution increases with rise in temperature.

(v) Presence of common ion: The degree of ionisation of an electrolyte decreases in the presence of a strong electrolyte having a common ion.

3. Explain the determination of transport number by moving boundary method.

The moving Boundary method rests on the direct observation of migration of ions in an electric field. The principle may be explained with reference to determination of transport number of H^+ hydrochloric acid. The conductivity cell in this method consists of a vertical tube of uniform bore filled with cadmium chloride and hydrochloric acid

Hydrochloric acid is the principle electrolyte while cadmium chloride serves as the indicator electrolyte to enable information of boundary.TheConcentration of the solutions are so adjusted that hydrochloric acid solution is s lighter than the cadmium chloride solution and therefore, floats over the cadmium chloride solution sharp boundary appears between the two solutions. The selection of the indicator electrolyte has to be made carefully.Its cation should not move faster than the cation whose transport number is to be determined and it should have the same anion as the principal electrolyte. Cadmium chloride fulfills both these requirements. The mobility of cadmium ion is less than that of hydrogen ion and it has a common anion with hydrochloric acid. The anode inserted at the bottom is a stick of cadmium metal while the cathode at the top is a platinum foil. When a small current is made to flow through the conductivity cell. The chloride ions move towards the anode while hydrogen ions followed by cadmium ions move towards the cathode. The boundary separating the two solution also moves upwards as indicated by an arrow Suppose the boundary moves through a distance l cm .Then the volume of the liquid that has moved up is lacm2 where A is the cross sectional area of the tube in cm^2.Let the concentration of the acid be c gram equivalents per liter.

Then the number of gram equivalents of H+ ions carried towards the cathode=

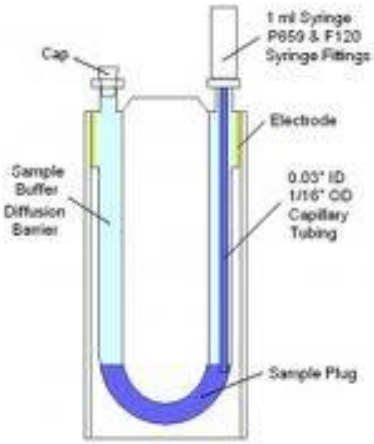
$$\frac{LaC}{1000}$$

Since each gram equivalent carries one faraday of electricity carried by H^+ions

$$= \frac{LaC}{1000} \text{ faradays}$$

Suppose the total current that flows in the same time as measured in a coulometer also included in the circuit =Q faradays

$$\text{Transport number of H+ ions} = \frac{LaC}{1000} \text{ faradays}$$



4. Write note on conductometric titration.

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of t he solution varies during the course of titration. The equivalence point may be located

Graphically by plotting the change in conductance as a function of the volume of titrant added. In order to reduce the influence of errors in the conductometric titration to a minimum, the angle between the two branches of the titration

Curve should be as small as possible (see Fig. 6.2)

If the angle is very obtuse e, a small error in the conductance data can cause a large deviation. The following approximate rules will be found useful.

- The smaller the conductivity of the ion which replaces the reacting ion, the more accurate will be the result. Thus it is preferable to titrate a silver salt with lithium chloride rather than with HCl. Generally cations should be titrated with lithium salts and anions with acetates as these ions have low conductivity

- The larger the conductivity of the anion of the reagent which reacts with the

Cation to be determined, or vice versa, the more acute is the angle of titration Curve.

- The titration of a slightly ionized salt does not give good results, since the

Conductivity increases continuously from the commencement. Hence, the salt

Present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte.

- Throughout a titration the volume of the solution Is always increasing, unless the conductance is corrected for this effect, non linear titration curves result. The Correction can be accomplished by multiplying the observed conductance either by total volume $(V + V')$ or by the factor $(V + V')/V$, where V is the initial volume of solution and V' is the total volume of the reagent added.

The correction presupposes that the conductivity is a linear function of dilution; this is true only to a first approximation.

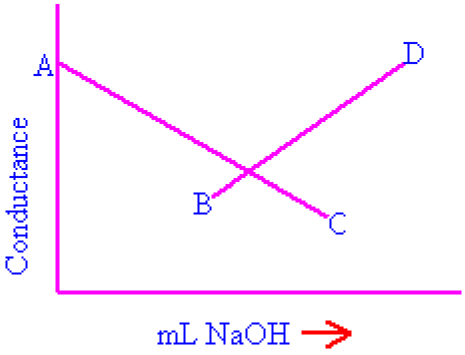
- In the interest of keeping V small, the reagent for the conductometric titration is ordinarily several times more concentrated than the solution being titrated (at Least 10-20 times). A micro burette may then be used for the volumetric measurement. The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to system that involve relative incomplete reactions. For example, which neither a potentiometric, nor indicator method can be used for the neutralization titration of phenol (K a = 10 – 0) a conductometric endpoint can be successfully applied. Application: Acid-base titration, especially at trace levels. Relative precision better than1% at all levels. There are also few disadvantages with this technique. As you know the conductance is a non-specific property, concentration of other electrolyte can be troublesome. The electrical conductance of a solution is a measure of its currents carrying capacity and therefore determined by the total ionic strength. It is a non-specific property and for this reason direct conductance measurement are of little use unless the solution contains only the electrolyte to be determined or the concentrations of other ionic species in the solution are known. Conductometric titrations, in which the species in the solution are converted to non-ionic for by neutralization, precipitation, etc. are of more value. 69 Applications of Conductometry, Electrogravimetry and Coulometry

Some Typical Conductometric Titration Curves are:

1. Strong Acid with a Strong Base, e.g. HCl with NaOH:

Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H + ions react with OH − ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl.

After the equivalence point, the conductance increases due to the large conductivity of OH - ions



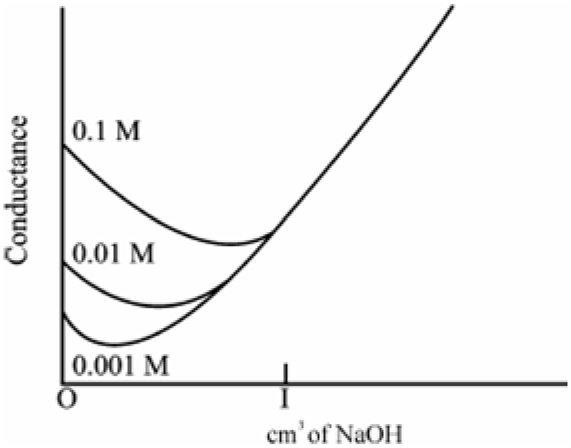
Conductometric titration of a strong acid (HCl) vs. a strong base

(NaOH)

2. Weak Acid with a Strong Base, e.g. acetic acid with NaOH:

Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H + by Na + but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH3 COOH to

CH3 COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH3COONa. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH− ions



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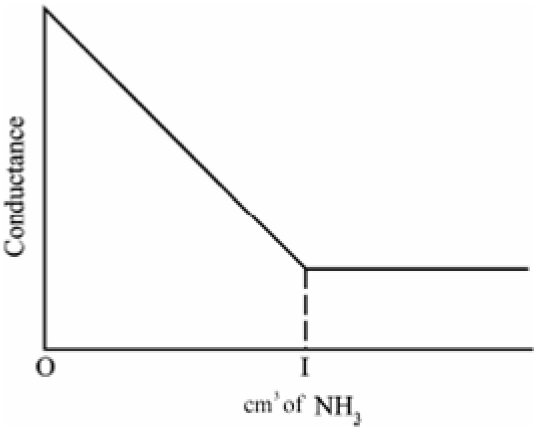
Conductometric titration of a weak acid (acetic acid) vs. a strong base

(NaOH)

3. Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia :

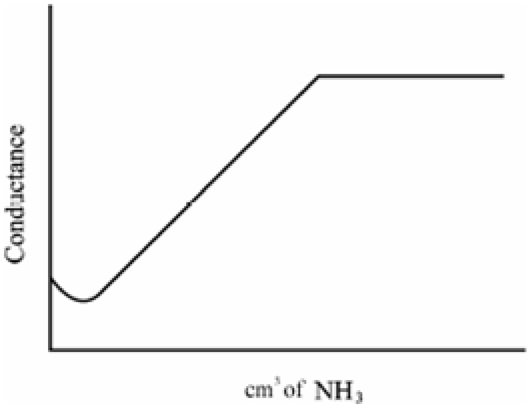
Initially the conductance is high and then it decreases due to the replacement of H+. But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the Presence of ammonium sulphate



Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)

4. Weak Acid with a Weak Base :

The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting (Fig. 6.5).



Conductometric titration of a weak acid (acetic acid) vs. a weak base

(NH_4OH)

5.Describe Debye huckel theory.

A description of Debye–Hückel theory includes a very detailed discussion of the assumptions and their limitations as well as the mathematical development and applications.

A snapshot of a 2-dimensional section of an idealized electrolyte solution is shown in the adjacent picture. The ions are shown as spheres with unit electrical charge. The solvent (pale blue) is shown as a uniform medium, without structure. On average, each ion is surrounded more closely by ions of opposite charge than by ions of like charge. These concepts were developed into a quantitative theory involving ions of charge z_1e^+ and z_2e^-, where z can be any integer. The principal assumption is that departure from ideality is due to electrostatic interactions between ions, mediated by coulombs law the force of interaction between two electric charges, separated by a distance, r in a medium of relative permittivity $_r$ is given by

$$\text{force} = \frac{z_1 z_2 e^2}{4\pi\epsilon_0\epsilon_r r^2}$$

It is also assumed that

- The solute s completely dissociated; it is a strong electrolyte. Ions are spherical and are not polarized by the surrounding electric field. Solvation of ions is ignored except insofar as it determines the effective sizes of the ions.
- The solvent plays no role other than providing a medium of constant relative permittivity (dielectric constant).
- There is no electrostriction.
- Individual ions surrounding a "central" ion can be represented by a statistically averaged cloud of continuous charge density, with a minimum distance of closest approach.

The last assumption means that each cation is surrounded by a spherically symmetric cloud of other ions. The cloud has a net negative charge. Similarly each anion is surrounded by a cloud with net positive charge.

Mathematical development

Debye–Huckel equation

The deviation from ideality is taken to be a function of the potential energy resulting from the electrostatic interactions between ions and their surrounding clouds. To calculate this energy two steps are needed.

The first step is to specify the electrostatic potential for ion *j* by means of

Poisson's equation

$$\nabla^2\psi_j(r) = -\frac{1}{\epsilon_0\epsilon_r}\rho_j(r)$$

Ψ(*r*) is the total potential at a distance, *r*, from the central ion and ρ(*r*) is the averaged charge density of the surrounding cloud at that distance. To apply this formula it is essential that the cloud has spherical symmetry, that is, the charge density is a function only of distance from the central ion as this allows the Poisson equation to be cast in terms of spherical coordinates with no angular dependence.[

The second step is to calculate the charge density by means of a

Maxwell–Boltzmann distribution.

$$n_i' = n_i \mathrm{exp}\left(\frac{-z_i e\psi_j(r)}{kT}\right)$$

This distribution also depends on the potential ψ(*r*) and this introduces a serious difficulty in terms of the superposition principle. Nevertheless, the two equations can be combined to produce the

Poisson–Boltzmann equation.

$$\nabla^2\psi_j(r) = -\frac{1}{\epsilon_0\epsilon_r}\sum_i\left\{n_i(z_i e)\mathrm{exp}\left(\frac{-z_i e\psi_j(r)}{kT}\right)\right\}$$

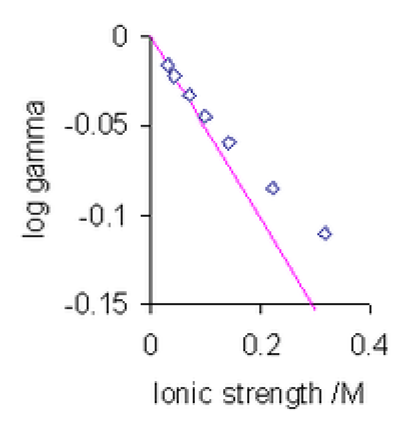
Solution of this equation is far from straightforward. It can be solved by successive approximations using modern electronic computers, but these were not available to

Debye and Hückel. Instead they expanded the exponential as a truncated Taylor series. This results in the truncated Poisson–Boltzmann equation,

$$\nabla^2\psi_j(r) = \frac{d^2}{dr^2}\psi_j(r) = \kappa^2\psi_j(r)$$

Which is a type of differential equation which has an analytical solution. This equation applies to 1:1, 2:2 and 3:3 electrolytes; for unsymmetrical electrolytes another term in ψ^2must be included. Incidentally, the truncated expansion may also remove the difficulty with the superposition principle.

The solution for a symmetrical electrolyte, in terms of the mean activity coefficient is given as



Experimental log $\gamma_\pm$ values for KBr at 25°C (points) and Debye–Hückel limiting law (colored line)

$$\log_{10}\gamma_\pm = -Az_i^2\frac{\sqrt{I}}{1+Ba_0\sqrt{I}}$$

$$A = \frac{e^2B}{2.303\times 8\pi\epsilon_0\epsilon_r kT}$$

$$B = \left(\frac{2e^2N}{\epsilon_0\epsilon_r kT}\right)^{1/2}$$

I is the ionic strength and a_0 is a parameter which represents the distance of closest approach of ions. For aqueous solutions at 25 °C $A = 0.51\ \text{mol}^{-1/2}\text{dm}^{3/2}$ and $B = 3.29\ \text{nm}^{-1}\text{mol}^{-1/2}\text{dm}^{3/2}$The most significant aspect of these algebraic manipulations is the prediction that the mean activity coefficient is a function of ionic strength. Of course the ionic strength of a 1:1 electrolyte is equal to its concentration, but that is not true for other types of electrolyte. Generally, activity coefficients are discussed in terms of ionic strength rather than the electrolyte concentration. For very low values of the ionic strength the value of the denominator in the expression above becomes nearly equal to one. In this situation the mean activity coefficient is proportional to the square root of the ionic strength. This is known as the Debye–Hückel limiting law.

6. Discuss the selection rule for vibrational transition.

Infrared light is absorbed only when a change in dipole character of the molecule takes place complete symmetry about a bond eliminates some absorption bands. Clearly, some of the fundamental vibrations are infrared active and some are not. It is governed by the selection rules.

(i) If a molecule has a centre of symmetry then the vibrations are centrofsymmetric and are inactive in the infrared but are active in the raman.

(ii) The vibrations which are not centre of symmetric are active in infrared but inactive in Raman.

Since in most of the organic compounds the functional groups are not conrosymmetric. Infrared spectroscopy is most informative. Consider various vibrations incase of co2

The above vibrations are all fundamental vibrations of CO_2. Since

(i) Does not give rise to any change in dipole moment, It is infrared in active.

(ii) An asymmetric stretching cause, a net change in dipole moment and thus are infrared active and absorbs at 2350 cm vibrations and are said to be degenerate.

(iii) The bending of bonds in the molecule are identical but occurs in perpendicular Planes and thus appear in the same position in the spectrum.

(iv) The spectrum of co2 consist of two bands

a. 2350cm due to asymmetric stretching
b. 667 cm due to bending vibrations.

7. Explain the Debye Falkenhagen effect?

Debye and falkenhagen examined the conductance behavior of a solution of a strong electrolyte by applying alternating current of different frequencies. The predicted that of the frequency of alternating current is high so that the time of oscillation is small in comparison with the relaxation time of the ionic atmosphere the asymmetry effect will be virtually absent.

In other words the ionic atmosphere around the central ion will remain symmetric. The rotating effect due to asymmetry may. Therefore be entirely absent and the conductance may be higher.

The conductance of a solution therefore should vary with the frequency of the alternating current used.

The higher the frequency the higher the conductance evidently. This effect also known as “dispersion of conductance” has been verified experimentally.

The conductance remains independent of the frequency of alternating current up to 10 cycles per second. But with further increase in frequency the conductance starts increase towards a certain limiting value indicating effect.

Thus the conductance of a strong electrolyte in aqueous solution increase in potential gradient applied. This observation has been verified experimentally by wein much before the development of the theory of strong electrolyte and is known as wein effect.

8. Derive on expression for Liquid junction potential and Thermodynamics of reversible reaction.

a) Liquid junction potential.

Liquid junction potential occurs when two solutions of different concentrations are in contact with each other. The more concentrated solution will have a tendency to diffuse into the comparatively less concentrated one. The rate of diffusion of each ion will be roughly proportional to its speed in an electric field. If the anions diffuse more rapidly than the cations, they will diffuse ahead into the dilute solution, leaving the latter negatively charged and the concentrated solution positively charged. This will result in an electrical double layer of positive and negative charges at the junction of the two solutions. Thus at the point of junction, a potential difference will develop because of the ionic transfer. This potential is called liquid junction potential or diffusion potential. The magnitude of the potential depends on the relative speeds of the ions' movement.

The liquid junction potential cannot be measured directly but calculated. The Electromotive force (EMF) of a concentration cell with transference includes the liquid junction potential.

Calculation

$E_{\text{without transference}} = RT/F. \ln (a_2/a_1)$

Where a_1 and a_2 are activities of HCl in the two solutions, R is the Universal Gas Constant, T is the temperature and F is Faraday's Constant.

$E_{\text{with transference}} = t_M\, RT/F . \ln (a_2/a_1)$

Where a_2 and a_1 are activities of HCl solutions of right and left hand electrodes respectively and t_M be transport number of Cl^-

Liquid Junction potential = $E_{\text{with transference}} - E_{\text{without transference}} =$

$(t_M - 1)\, RT/F . \ln (a_2/a_1)$

b) Thermodynamics of reversible cells

From Gibb's –Helmholtz equation,

$\Delta G=\Delta H+T[\partial(\Delta G/\Delta H)]p$ -------(1)

The relation between and ΔG, $\Delta G = -nFE$ ----(2)

On differentiation with respect to temperature,

$[\partial(\Delta G/\Delta H)]p = -nf[\partial E/\partial T]p$ ------(3)

Substituting eq.(3) and (2) in eq.(1) ,

$-nFE= -nFT [\partial E/\partial T]p$

.. $\Delta H = -nFE+nFT [\partial E/\partial T] p == nF\{T[[\partial E/\partial T]p-E\}$-------(4)

$[\partial E/\partial T] p$ is known as the temperature coefficient of EMF.

We know that $\Delta H = \Delta G+T\Delta S$ -------- (5)

Comparisons of eqs.(5) and (4) gives

$T\Delta S = nFT [\partial E/\partial T]p$ and hence $\Delta S = nF[\partial E/\partial T]p$--------(6)

The entropy change of a reaction can be calculated from the temperature co-efficient

9. What is meant by standard electrode potential?

If in an electrode set up, all active constituents or reactants are at unit activity, it is said to be normal or standard electrode. This can be achieved, when the concentration of the electrolyte taken is one molar and the electrode is a pure solid or gas at a pressure of one atmosphere. The electrode is set up at a temperature of 298K. The electrode potential. It is denoted by E^O, such an electrode is called standard or normal electrode. For example, a standard zinc electrode is set up by dipping a zinc metal rod into one molar zinc sulphate solution kept at 298K and one atmosphere pressure. It can be represented ad $Zn(s)/Zn^{+2}$ (1M).

The electrode potential developed in a standard electrode due to oxidation reaction taking place on the electrode in a galvanic cell is called standard oxidation electrode potential and is denoted by E^o oxidation,. Similarly, the electrode potential developed in a standard electrode due t reduction reaction taint place on the electrode in a galvanic cell is called standard reduction electrode potential and is denoted by E^o reduction. Since the reduction half reaction is just the reverse of oxidation half reaction, therefore reduction potential is obtained from oxidation potential by simply changing the sin for any electrode as these are equal in magnitude but opposite in direction. So $E^o_{red} = - E^o_{oxi}$

It is important to mention here that is a convention tom express all electrode potential as per the recommendations of IUPAC .Therefore, E_{red} may be expressed as E only and stand and free energy c E^o_{red} as $E^o_{.}$

10. Derive on Nernst equation from reversible reaction

From the reaction isotherm, the free energy (ΔG) for the cell reaction

$\Delta G = - RT \ln Kc + RT\Delta v \ln a$

Where Kc is the equilibrium constant and 'a' terms denote activities

$\Delta G^0 = -RT \ln Kc$

$\Delta G = - \Delta G^0 + RT\Delta v \ln a$

If E is the emf of the cell in the given state and E^0 is the standard emf of the cell, then

$\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$

$-nfe = -nFE^0 + RT\Delta v \ln a$ (or)

$$E = E^0 - RT/nF\ \Sigma v \ln a = E^0 - 2.303RT/nF \log \frac{[\text{activities of product}]}{[\text{activities of reactant}]}$$

This equation is called the Nernst equation. E^0 is the EMF of the cell at standard conditions, n is the number of electrons involved, F is the Faraday equal to 96500 coulombs, T is temperature in Kelvin, and R is the gas constant in joules, 8.314. At 25^0C, 2.303RT/F=0.059 and the equation becomes

1. $E = E^0 - 0.0591/n \log \dfrac{[\text{activities of product}]}{[\text{activities of reactant}]}$

If the cell reaction is $aA+bB \rightleftharpoons lL+mM$, the above equation can be written in terms of single electrode potentials as

$E = [E_1^0 - RT/nF\Delta \ln a_1^{v1}] - [E_2^0 - RT/nF\Delta \ln a_2^{v2}]$

E_1^0 and E_2^0 are the standard single electrode potentials,

a_1&a_2 are the activity terms and

v_1& v_2 are the no. of molecules or ions involved in the corresponding electrode reaction.

11. The EMF of standard Weston cell written $CdSo_4$ (sat), Hg2So4(s), Hg in which cell reaction is

Cd (Hg), $CdSo_4$ (sat). 8/3H2O(s)//, CdSo4 (sat), Hg_2So_4(s), Hg in which cell reaction is

Cd (Hg) +Hg_2So_4(s) +8/3H_2O (l) $CdSo_4$. 8/3H_2O(s)+2Hg(l)

Is 1.0185v at 25^0c calculate ΔG^0, ΔS^0 , & ΔH^0 for the all reaction if $(\partial E^0/\partial T)p$ for the cell is 5.00 $10^{-5}VK^{-.}$ F=9685$Cmol^{-1}$

Solution.

1. Standard free energy change ΔG^0,

$\Delta G^0 = -nFE^0$

$= -2(96485Cmol^{-1})$ m (1.0813V)

$= -196501.3$ J =-196.501KJ

1. Standard entropy change ΔS^0

$\Delta S^0 = nF(\partial E^0/\partial T)$

$= 2(96485C \times (5.00\times10^{-}5VK^{-1})$

$= 9.65JK^{-1}$

2. Standard enthalpy change ΔH^0

$\Delta H^0 = \Delta G^0 + T\Delta S^0$

$= \quad -196501J\times(298K)(9.65JK^{-1})$

$= \quad -193625J=-193.6KJ.$

12. What is the function of salt bridge cell?

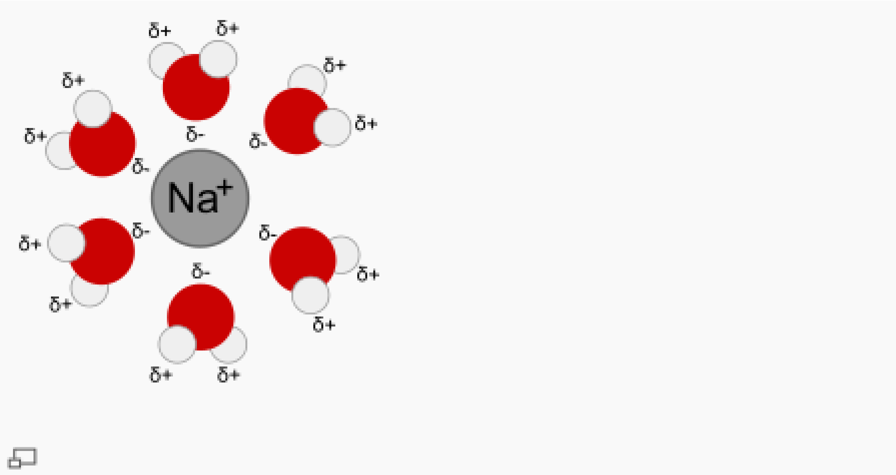
The salt bridge serves three important functions in a galvanic cell;

(i) It prevents any net chare accumulation in other beaker by permitting the excess of ions to diffuse from one half cells to other through the salt bridge. Thus, it maintains electrical neutrality in the two half cells.

(ii) It physically separates the two electrodes, but completes the electrical circuit with electrons flowing from one electron to another externally and the ions flow in between the two compartments through salt bridge.

(iii) It minimizes the liquid functions potential between the two solutions connected through salt brid

13. Explain the Limitations and extension of Debye Heckle theory.



The first solvation shell of a sodium ion dissolved in water. The oxygen atoms are arranged at the vertices of an octahedron with the sodium ion at its centre

The equation for log $\gamma\pm$ gives satisfactory agreement with experimental measurements for low electrolyte concentrations, typically less than 10^{-3} mol dm^{-3}. Deviations from the theory occur at higher concentrations and with electrolytes that produce ions of higher charges, particularly unsymmetrical electrolytes. Essentially these deviations occur because the model is hopelessly oversimplified, so there is little to be gained making small adjustments to the model. The individual assumptions can be challenged in turn.

Complete dissociation. Ion-association may take place, particularly with ions of higher charge. This was followed up in detail by Niles Bjerrum. The Bjerrum length is the separation at which the electrostatic interaction between two ions is comparable in magnitude to kT.

Weak electrolytes. A weak electrolyte is one that is not fully dissociated. As such it has a dissociation constant. The dissociation constant can be used to calculate the extent of dissociation and hence, make the necessary correction needed to calculate activity coefficients

Ions are spherical and are not polarized. Many ions such as the nitrate ion, NO_3^-, are manifestly not spherical. Polyatomic ions are also polarizable.

Role of the solvent. The solvent is not a structure less medium but is made up of molecules. The water molecules in aqueous solution are both dipolar and polarizable. Both cations and anions have a strong primary solvation shell and a weaker secondary solvation shell. Ion-solvent interactions are ignored in Debye–Heckle theory.

Moreover, we assume that the ionic radius is negligible, but at higher concentrations, the ionic radius becomes comparable to the radius of the ionic cloud. Most extensions to Debye– Hackle theory are empirical in nature. They usually allow the Debye–Hückel equation to be followed at low concentration and add further terms in some power of the ionic strength to fit experimental observations. The main extensions are the Davies equation, Pitzer equations and Specific ion interaction theory

14. Explain the construction of C3v C3haracter table

There are three classes of operation there should be three equal irreducible representation r1, r2, and r3.

The sum of the square to t .Therefore should be two one dimensional and one two dimensional representation .So that,

1+1+2 =6

1+1+4 =6

The irreducible representation with the character of identity operation

C3v	E	2C3	3v
r1	1	1	1
r2	1	x	y
r3	2	a	b

For any point group there should be one irreducible representation which is symmetrical to all the operations. That is the character corresponding to all the operation is +1.

C3v	E	2C3	3 v
r1	1	1	1

1+2(1) +3(1) =6

The sum of the square of the character of the operation is equal to 6.

1+2(1) +3(1) =6

The character of the two irreducible representation are orthogonal to each other .Let x &y represent the character of the C3 & v operation in the irreducible representation r2.

C3v	E	2C3	3v
r1	1	1	1
r2	1	x	y
r3	1		

If r1&r2 are orthogonal.

$1.1.1+2.1.x+3.1.y=0$

The above equations can be correct only when the values of x=1,

Y=-1, thus the character of r2 represents,

C3v	E	2C3	3v
r1	1	1	1
r2	1	1	-1
r3	1	a	b

The character of r3 should be orthogonal to r1&r2 and the character of identity operation is 2.Let a&b represent the character of C3&v operation in the reducible representation are 3 if r1&r2 orthogonal.

r1&r3

$1(1)\ (2)\ +2(1)\ (a)\ +3(1)\ (b)\ =0$

$2+2(a)\ +3(b)\ =0$

$2a+3b=-2$ (1)

r2&r3

$1(1)\ (2)\ +2(1)\ (a)\ +3(-1)\ b=0$

$2+2a-3b=0$

$2a-3b=-2$ (2)

From equation (1) & (2) we get

$a=-1,\ b=0$

$2(-1)-3(0)\ =-2$

$-2-0=-2\ =1$

C3v	E	2C3	3v	
R1	1	1	1	(x2, y2)
R2	1	1	-1	Rxy
R3	2	-1	0	(xy) (yx)

R1 irreducible representation of one dimensional symmetrical to the principle axis and to the vertical plane .it is denoted A1.

R2 is also one dimensional but it is asymmetrical with respect to the vertical plane hence the symbol is A2.

R3-is two dimensional and the symbol is E.

15. Derive the Photo chemical reaction between H_2 &Br_2

$H_2 + Br_2 \rightarrow 2HBr$

$d[HBr]/dt = K'[H_2][I_2]/1 + [HBr]/m'[Br_2]$

$Br_2 \rightarrow 2Br$ ……….. ……… (1)

$Br + H_2 \rightarrow HBr + H$ ………………… (2)

$H + Br_2 \rightarrow HBr + Br$ ………………. (3)

$H + HBr \rightarrow H_2 + Br$ ……………….. (4)

$Br + Br \rightarrow Br_2$ ……………….. (5)

The photochemical reaction between H_2 and Br_2 proceeds according to the empirical equation. Where K’ and m’ are constant I is intensity of the radiation or light absorbed .Only different between the thermal and photochemical process.

The photochemical process the Br_2 radicals are produced by absorption of photons by bromine molecule.

d[Br]/dt=2I-K2[I2][Br]+K3[H][Br_2]+K4[H][H Br]-K5[Br]2 =0 (1)

d [H]/dt =K2[H_2][Br]-K3[H][Br_2]-K4[H][H Br] =0 (2)

Adding equation (1) & (2)

2I =K5[Br]2

[Br] = [k5/2I]1/2 (3)

Rearranging equation (2) we get,

K2 [H_2][BR] = [H]{K3[Br_2]+K4[H Br]}

[H] = K2 [H_2] [Br]/K3 [Br_2] +K4 [H Br] (4)

The rate of formation of H Br can be written as,

D[HBr]/dt = k2[H_2][Br]+k3[H][Br_2]-k4[H][H Br] (5)

K2 [H2][Br]+[H]{K3[Br2]-K4[H Br]} (6)

Substituting the value [H] from equation (4) in equation (6) we get,

d [H Br]/dt= K2[H_2][Br]+K2[H_2][Br]/K3[Br_2]+K2[H Br]{k3[Br2]-k4 [H Br]}

d [H Br]/dt =2k2[H_2][Br]k3[Br2]/k3[Br_2]+k4[HBr]

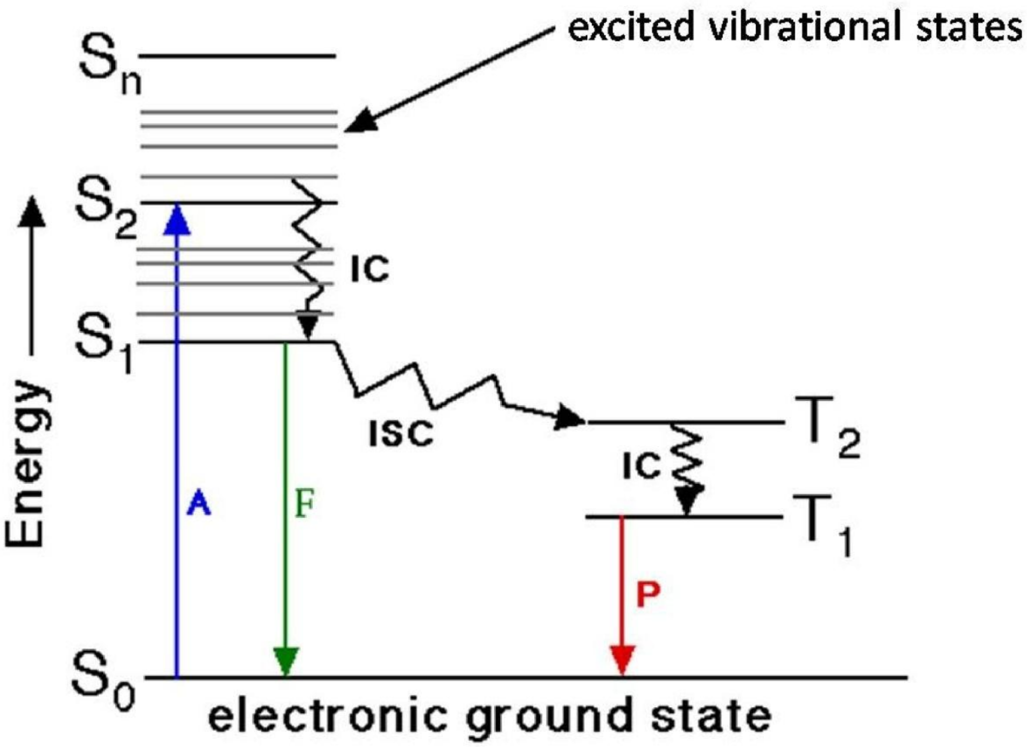
d [HBr] =2k2[H_2][Br]k3[Br_2]/1+K4[HBr]/k3[Br_2]

d [HBr]/dt=2(2I/K5)1/2 K2 [H_2]/1+K4 [HBr]/k5 [Br_2]

k’=2k2(k5)1/2 and m’=k3/k4

The rate of photochemical reaction is 300 times that of the thermal reaction at the same temperature

16.Explain the Jablonski Diagram.



Non-radiative transition:

This transition involve the return of the activated molecule from the higher excited state.[S2-S3]or[T3-T2].To the first excited state [S1-T1].This transition do not involve the emition of radiation and that term as non-radiative transition. The energy of the activated molecule is dizibated in the form of heat through molecular collusion.The process is called internal conversion[IC].The transition are also non-radiative spin-forbidden.Anaccur in less the above 10-11 sec.The molecule may also less energy by another process is called inter system crossing[ISC].Which involve transition between states of different spin.S2-T2,S1-T1,S2-S1,T2-T1.This transition are also non-radiative transition.

Radiative Transition:

The transition involve returns of the activated molecule from this singlet excited state.S1&T2.

Such transitions are accumbine by emission of radiation. This transition from S1->S0, is an spin allowed transition and accurs in above 10-8 sec.Theemision of radiation in this transition is called fluorescence.

The transition from triplet excited state T1 to the ground state so [T1-S0].It is spin forbidden .The emission of radiation in this transition is called phosphorescence. The life time of phosphorescence is much longer then the order of 10-3 sec and 10-7 sec.

17. Write short note on Phosphorescence.

A substance absorbs radiation of higher frequency and emits light even after he incident radiation is cut off the process is called phosphorescence.

The substance which phosphorescence is called phosphorescent substance.

EXAMPLE: sulphates of calcium, barium exhibit phosphorescence.

Flurescenes in blue region at 5700A wave length.

EXPLANATION:

A molecule absorb light variations and gets excited while returning to the ground state it emits light energy on longer wave length. The excited molecules passes from one series to another series of electronic state and gets trapped. The emission of light which persist even after the removal of light source.

18.Explain the C2v Point Group of water molecule.

C2v point group there are four operation .There are four irreducible representation r1, r2, r3, r4.Thesome of the square of the dimension of irreducible representation should be equal to four.

Example: H2O

Hence each dimension must be uni dimension.

1+1+1+1=4;

Since the dimension of the representation is equal to character of the identity element (or) operation of the irreducible representation E must be equal to 1 in all the terms.

The some of the square of characters of irreducible representation must be equal to four

So for one of irreducible representation (r1) all the characters must be 1.

C2v	E	C2	v	v'
r1	1	1	1	1
r2	1			
r3	1			
r4	1			

In case of other irreducible representation the some of the square of character must be equal to four. The character must be orthogonal two (or)one.The character must include two +1,two-1.

C2v	E	C2	v	v'
r1	1	1	1	1
r2	1	1	-1	-1
r3	1	-1	1	-1
r4	1	-1	-1	1

Uni dimensional – A, B

Two dimensional –E

Three dimensional-T are called difference symbol.

On the basis of above points symbols can be assign to the irreducible representation of C2v point group.r1 is one dimensional symmetrical to the principal axes and the vertical plane v(xz).Hence the symbol is A. r2 is irreducible representation symmetrical to principal axis but unsymmetrical v(xz),hence the symbol is A2.r3 –one dimensional unsymmetrical to principle axis but symmetrical with respect to v(xz) .Hence the symbol is B1.r4 is one dimensional unsymmetrical to the principle axis .symbol is B2. V (xz).

	C2v	E	C2	v	v'		
A1	r1	1	1	1	1	Z	x2y2z2
A2	r2	1	1	-1	-1	Rzxy	
B1	r3	1	-1	1	-1	x,Ryxz	
B2	r4	1	-1	-1	1	y,Rxzy	

19. Derive lamberts-beer law

When a beam of monochromatic light travels a homogeneous absorbing medium the intensity of the incident light decreases exponentially with thickness of the medium as well as the concentration of the solution

In other words this law can be stated as the rate of decrease of incident light intensity with thickness of the absorbing medium is proportional to the intensity of incident light as well as the concentration of the solution.

$$\frac{-dI}{dl} = \frac{k'}{C}$$

$I -$ Intensity of the incident light .
$dl -$ Thickness
$c -$ Concentration of the solution
$k' -$ Constant or the molar absorption coefficient
On rearranging and integrating we get,
$ln\frac{I}{I_0} = -k'cl$ or I=$I_0 e^{-kct}$

Changing the equation to logarithm to the base of 10 we get ‘

A=£cl

Where

A - Called absorbents

£ - molar extinction coefficient

20. Distinguish between photochemical and thermal reaction.

Photochemical reaction	Thermal reaction
1. These involve absorption of light radiations. 2.The presence of light is the primary requirement for reactions to take place 3. Temperature has a very little effect on the rate of Photochemical reactions. 4. G for photochemical spontaneous reactions may be (+)ve or(-)ve 5. Photochemical activation is highly selective. The absorbed photon excites a particular atom or group of atoms which become site for the reaction.	These reactions involve absorption or evolution of Heat. These reactions can take place in dark as well as in light. Temperature has a significant effect on the rate of a thermo chemical reaction. G for a thermo chemical reaction is always (-)ve Thermo chemical activation is not selective in nature.

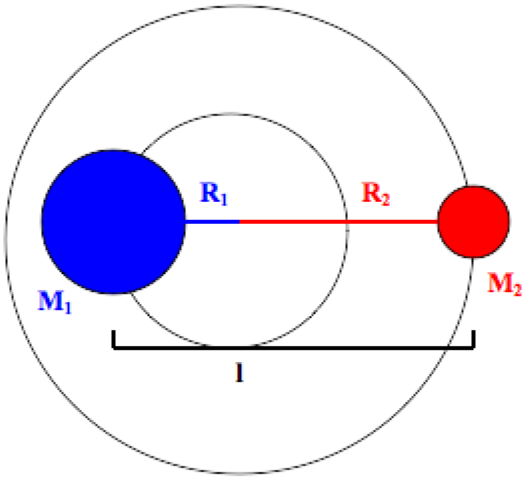
21. Describe the types of symmetry elements.

The symmetry of a molecule can be described by 5 types of symmetry elements.

- **Symmetry axis**: an axis around which a rotation by $\frac{360°}{n}$ results in a molecule indistinguishable from the original. This is also called an *n*-fold **rotational axis** and abbreviated C_n. Examples are the C_2 in water and the C_3 in ammonia. A molecule can have more than one symmetry axis; the one with the highest *n* is called the **principal axis**, and by convention is assigned the z-axis in a Cartesian coordinate system.
- **Plane of symmetry**: a plane of reflection through which an identical copy of the original molecule is given. This is also called a mirror plane and abbreviated σ. Water has two of them: one in the plane of the molecule itself and one perpendicular to it. A symmetry plane parallel with the principal axis is dubbed *vertical* (σ_v) and one perpendicular to it *horizontal* (σ_h). A third type of symmetry plane exists: If a vertical symmetry plane additionally bisects the angle between two 2-fold rotation axes perpendicular to the principal axis, the plane is dubbed dihedral (σ_d). A symmetry plane can also be identified by its Cartesian orientation, e.g., (xz) or (yz).
- **Center of symmetry** or **inversion center**, abbreviated *i*. A molecule has a center of symmetry when, for any atom in the molecule, an identical atom exists diametrically opposite this center an equal distance from it. There may or may not be an atom at the center. Examples are xenon tetrafluoride where the inversion center is at the Xe atom, and benzene (C_6H_6) where the inversion center is at the center of the ring.
- **Rotation-reflection axis**: an axis around which a rotation by $\frac{360°}{n}$, followed by a reflection in a plane perpendicular to it, leaves the molecule unchanged. Also called an *n*-fold **improper rotation axis**, it is abbreviated S_n. Examples are present in tetrahedral silicon tetrafluoride, with three S_4 axes, and the staggered conformation of ethane with one S_6 axis.
- **Identity**, abbreviated to E, from the German 'Einheit' meaning unity. This symmetry element simply consists of no change: every molecule has this element. While this element seems physically trivial, it must be included in the list of symmetry elements so that they form a mathematical group. Whose definition requires inclusion of the identity element. It is so called because it is analogous to multiplying by one (unity).

22. Explain the rigid rotator of diatomic molecule.

A diatomic molecule consists of two masses bound together. The distance between the masses, or the bond length, (l) can be considered fixed because the level of vibration in the bond is small compared to the bond length. As the molecule rotates it does so around its COM (observed in Figure 1. as the intersection of $R1$ and $R2$) with a frequency of rotation of $vrot$ given in radians per second.



Rigid Rotor Model of a Diatomic Molecule

Reduced mass

The system can be simplified using the concept of reduced mass which allows it to be treated as one rotating body.

1.) The system can be entirely described by the fixed distance between the two masses instead of their individual radii of rotation. Relationships between the radii of rotation and bond length are derived from the COM given by: $M1R1=M2R2$, where l is the sum of the two radii of rotation: $l=R1+R2$.

2.) Through simple algebra both radii can be found in terms of their masses and bond length: $R1=M2M1+M2l$ and $R2=M1M1+M2l$.

3.) The kinetic energy of the system, T, is sum of the kinetic energy for each mass: $T=M1v21+M2v222$, where $v1=2\pi R1vrot$ and $v2=2\pi R2vrot$.

4.) Using the angular velocity, $\omega=2\pi vrot$, the kinetic energy can now be written as: $T=M1R21+M2R222\omega$.

5.) With the moment of inertia, $I=M1R21+M2R22$, the kinetic energy can be further simplified: $T=I\omega22$.

6.) The moment of inertia can be rewritten by plugging in for R_1 and R_2: $I=M1M2M1+M2l2$, where $M1M2M1+M2$ is the reduced mass, μ.

7.) The moment of inertia and the system are now solely defined by a single mass, μ, and a single length, l: $I=\mu l2$.

Angular momentum

Another important concept when dealing with rotating systems is the the angular momentum defined by: $L=I\omega$

Looking back at the kinetic energy: $T=I\omega22=I2\omega22I=L22I$

The angular momentum can now be described in terms of the moment of inertia and kinetic energy: $L2=2IT$.

1.) The wave functions for the rigid rotor model are found from solving the Schrodinger Equation: $H\text{^}\psi=E\psi$

2.) Where the Hamiltonian Operator is: $H\text{^}=-\hbar 2\mu\bigtriangledown 2+V(r)$

$\bigtriangledown 2$ is known as the Laplacian Operator and can be represented in either cartesian coordinates:

$\bigtriangledown 2=\partial 2\partial x2+\partial 2\partial y2+\partial 2\partial z2$

or in spherical coordinates:

$\bigtriangledown 2=1r2\partial\partial r(r2\partial\partial r)+1r2\sin\theta\partial\partial\theta(\sin\theta\partial\partial\theta)+1r2\sin2\theta\partial 2\partial\phi$

At this point it is important to incorporate two assumptions:

a.) The distance between the two masses is fixed. This causes the terms in the Laplacian containing ∂∂r to be zero.

b.) The orientation of the masses is completely described by θ and ϕ and in the absence of electric or magnetic fields the energy is independent of orientation. This causes the potential energy portion of the Hamiltonian to be zero.

The wave functions \psi{\left(\theta,\phi\right) are customarily represented by Y(θ,ϕ) and are called spherical harmonics.

3.) The Hamiltonian Operator can now be

written: H^=T^=−ℏ22μl2[1sinθ∂∂θ(sinθ∂∂θ)+1sinθ∂2∂ϕ2]

With the Angular Momentum Operator being defined:

a.) L^=2IT^

b.) L^=−ℏ2[1sinθ∂∂θ(sinθ∂∂θ)+1sinθ∂2∂ϕ2]

4.) And the Schrodinger Equation now

expressed: −ℏ22I[1sinθ∂∂θ(sinθ∂∂θ)+1sinθ∂2∂ϕ2]Y(θ,ϕ)=EY(θ,ϕ)

Solving the schrodinger wave equation

The Schrodinger Equation can be solved using separation of variables.

1.) Let, Y(θ,ϕ)=Θ(θ)Φ(ϕ), and substitute: β=2IEℏ2.

2.) Set the Schrodinger Equation equal to

zero: sinθΘ(θ)ddθ(sinθdΘdθ)+βsin2θ+1Φ(ϕ)d2Φdϕ2=0

3.) Because the terms containing $\Theta(\theta)$ are equal to the terms containing $\Phi(\phi)$ they must equal the same constant in order to be defined for all values:

a.) $\sin\theta\Theta(\theta)dd\theta(\sin\theta d\Theta d\theta)+\beta\sin 2\theta=m2$

b.) $1\Phi(\phi)d2\Phi d\phi 2=-m2$

3.) Solving for Φ is fairly simple and yields:

a.) $\Phi(\phi)=12\pi{-}{-}\surd eim\phi$, where $m=0,\pm1,\pm2,...$

Solving for θ is considerably more complicated but gives the quantized result:

b.) $\beta=J(J+1)$, where J is the rotational level and J=0, 1, 2,...

4.) The energy is quantized by expressing in terms of β: $E=\hbar 2\beta 2I$

5.) Using the rotational constant, $B=\hbar 22I$, the energy is further simplified: E=BJ(J+1)

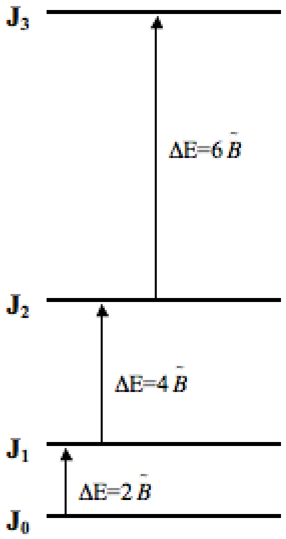
23. Explain the energy rotational transition.

When a molecule is irradiated with photons of light it may absorb the radiation and undergo an energy transition. The energy of the transition must be equivalent to the energy of the photon of light absorbed given by: $E=hv$. For a diatomic molecule the energy difference between rotational levels (J to J+1) is given by:

$EJ+1-EJ=B(J+1)(J+2)-BJ(J=1)=2B(J+1)$

With J=0, 1, 2,...

Because the difference of energy between rotational levels is in the microwave region (1-10 cm^{-1}) rotational spectroscopy is commonly called microwave spectroscopy. In spectroscopy it is customary to represent energy in wave numbers (cm^{-1}), in this notation B is written as B~. To convert from units of energy to wave numbers simply divide by h and c, where c is the speed of light in cm/s (c=2.998e10 cm/s). In wave numbers $B\text{~}=h8\pi cI$.



Rotational Energy Levels

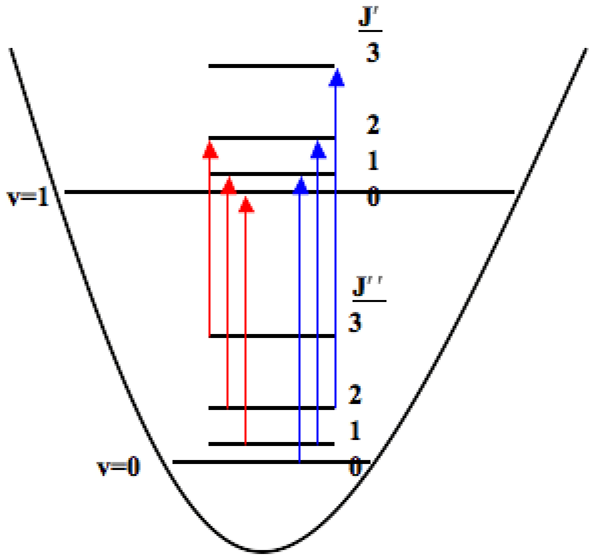
Figure 2 predicts the rotational spectra of a diatomic molecule to have several peaks spaced by 2{\tilde {B}. This contrasts vibrational spectra which have only one fundamental peak for each vibrational mode.

From the rotational spectrum of a diatomic molecule the bond length can be determined. Because {\tilde{B} is a function of I and therefore a function of l (bond length), l is readily solved for: $l=h8\pi 2cB\sim\mu$−−−−−−−−√.

Note: Selection rules only permit transitions between consecutive rotational levels: $\Delta J=J\pm 1$, and require the molecule to contain a permanent dipole moment. Due to the dipole requirement, molecules such as HF and HCl have pure rotational spectra and molecules such as H_2 and N_2 are rotationally inactive.

24. Write note on Rotational vibration transition.

Rotational transitions are on the order of 1-10 cm^{-1}, while vibrational transitions are on the order of 1000 cm^{-1}. The difference of magnitude between the energy transitions allow rotational levels to be superimposed within vibrational levels.



Rotation-Vibration Transitions

Combining the energy of the rotational levels, $E{\sim}J=B{\sim}J(J+1)$, with the vibrational levels, $E{\sim}v=w{\sim}(v+1/2)$, yields the total energy of the respective rotation-vibration levels:\tilde{E}_{v,J}=\tilde{w}\left({v+1/2\right)+\tilde{B}J(J+1).

Following the selection rule, $\Delta J=J\pm1$, Figure 3. shows all of the allowed transitions for the first three rotational states, where J" is the initial state and J' is the final state.

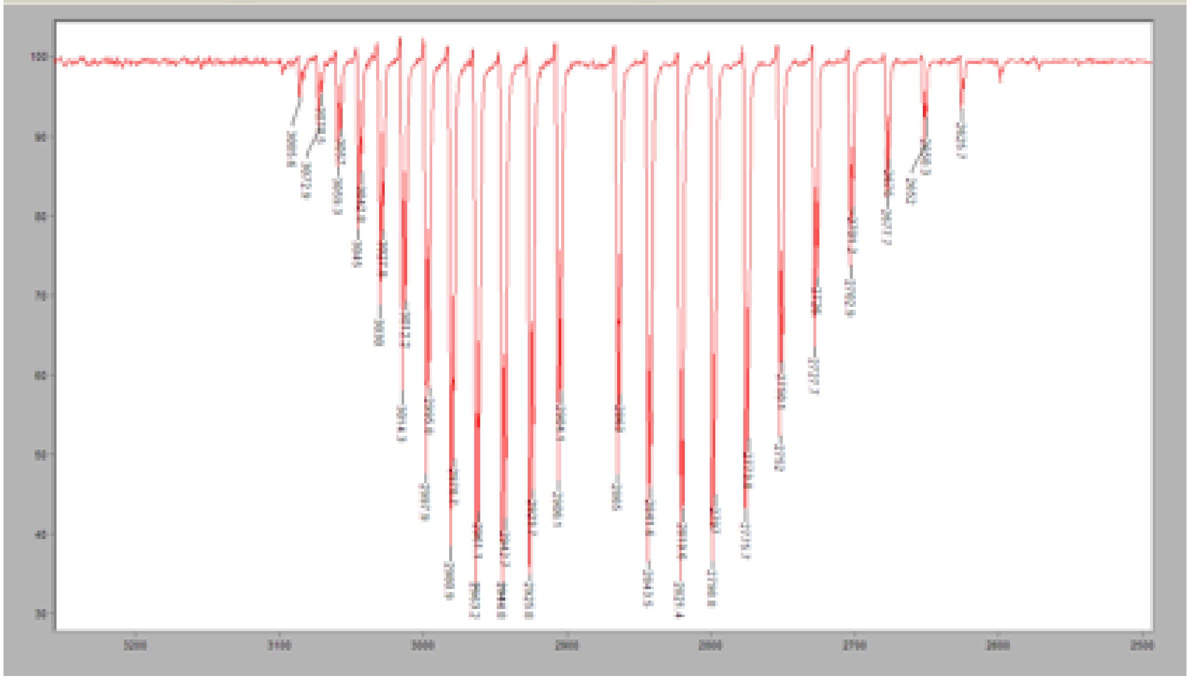
When the $\Delta J=+1$ transitions are considered (blue transitions) the initial energy is given by: $E{\sim}0,J=w{\sim}(1/2)+B{\sim}J(J+1)$ and the final energy is given by: $E{\sim}v,J+1=w{\sim}(3/2)+B{\sim}(J+1)(J+2)$.

> *The energy of the transition, $\Delta v{\sim}=E{\sim}1,J+1-E{\sim}0,J$, is therefore: $\Delta v{\sim}=w{\sim}+2B{\sim}(J+1)$ where J"=0, 1, 2,...

When the $\Delta J=-1$ transitions are considered (red transitions) the initial energy is given by: $E{\sim}v,J=w{\sim}(1/2)+B{\sim}J(J+1)$ and the final energy is given by: $E{\sim}v,J-1=w{\sim}(3/2)+B{\sim}(J-1)(J)$.

> *The energy of the transition is therefore: $\Delta v{\sim}=w{\sim}-2B{\sim}(J)$ where J"=1, 2, 3,...

The difference in energy between the J+1 transitions and J-1 transitions causes splitting of vibrational spectra into two branches. The J-1 transitions, shown by the red lines in Figure 3., are lower in energy than the pure vibrational transition and form the P-branch. The J+1 transitions, shown by the blue lines in Figure 3. are higher in energy than the pure vibrational transition and form the R-branch. Notice that because the ΔJ=\plusminus0 transition is forbidden there is no spectral line associated with the pure vibrational transition. Therefore there is a gap between the P-branch and R-branch, known as the q branch.



HCl Rotation-Vibration Spectrum

In the high resolution HCl rotation-vibration spectrum the splitting of the P-branch and R-branch is clearly visible. Due to the small spacing between rotational levels high resolution spectrophotometers are required to distinguish the rotational transitions.

Recall the Rigid-Rotor assumption that the bond length between two atoms in a diatomic molecule is fixed. However, the anharmonicity correction for the harmonic oscillator predicts the gaps between energy levels to decrease and the equilibrium bond length to increase as higher vibrational levels are accessed. Due to the relationship between the rotational constant and bond length:

B~$=h8\pi 2c\mu l2$

The rotational constant is dependent on the vibrational level:

$B{\sim}v=B{\sim}-\alpha{\sim}(v+12)$

Where $\alpha{\sim}$ is the anharmonicity correction and v is the vibrational level.

As a consequence the spacing between rotational levels decreases at higher vibrational levels and unequal spacing between rotational levels in rotation-vibration spectra occurs.

Including the rotation-vibration interaction the spectra can be predicted.

For the R-branch

$E{\sim}1,J+1-E{\sim}0,J$

$v{\sim}=[w{\sim}(32)+B{\sim}1(J+1)(J+2)]-[w{\sim}(12)+B{\sim}0J(J+1)]$

$v{\sim}=w{\sim}+(B{\sim}1-B{\sim}0)J2+(3B{\sim}1-B{\sim}0)J+2B{\sim}1$

where J=0, 1, 2,...

For the P-branch

$E{\sim}1,J-1-E{\sim}0,J$

$v{\sim}=[w{\sim}(32)+B{\sim}1(J-1)J]-[w{\sim}(12)+B{\sim}0J(J+1)]$

$v{\sim}=w{\sim}+(B{\sim}1-B{\sim}0)J2-(B{\sim}1+B{\sim}0)J$

where J=1, 2, 3,...

Because $B{\sim}1<B{\sim}0$,

As J increases:

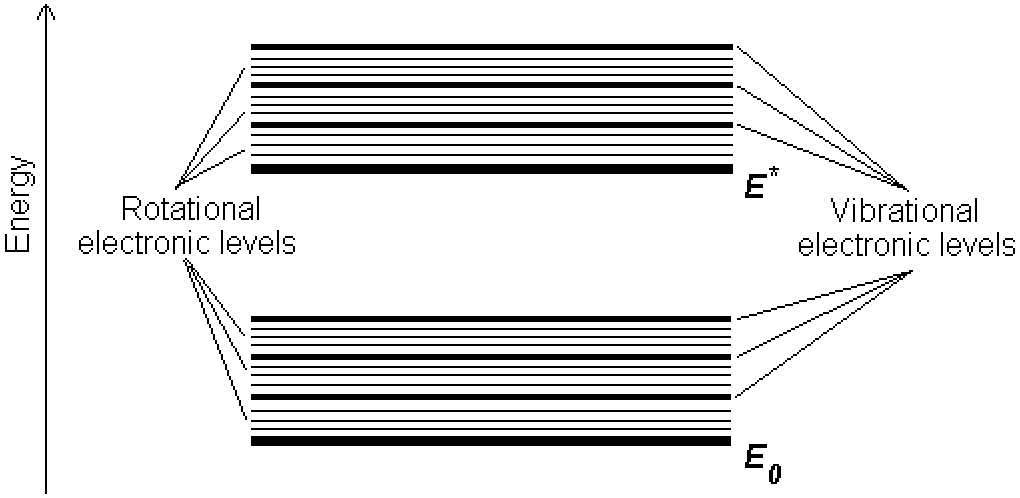
- Spacing in the R-branch decreases.
- Spacing in the P-branch increases.

25. Describe the Electronic transitions.

The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered;

1. Transitions involving π□ , □ , and *n* electrons
2. Transitions involving charge-transfer electrons
3. Transitions involving *d* and *f* electrons (not covered in this Unit)

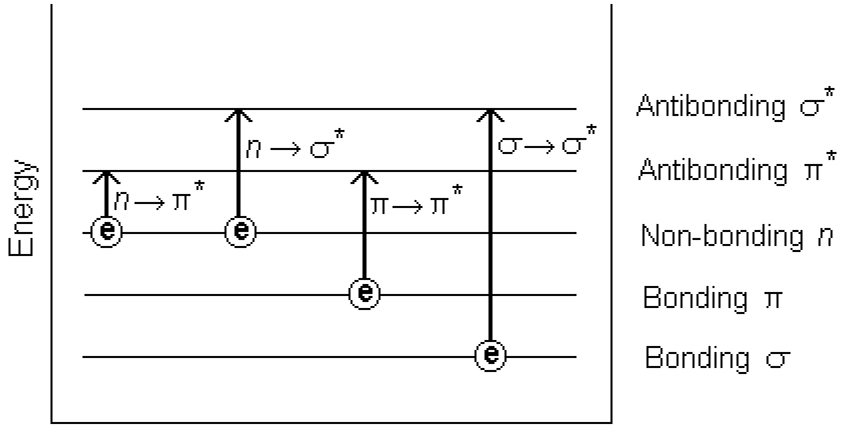
When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level.



Absorbing species containing □ , □ , and n electrons

Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups (*chromophores*) that contain valence electrons of low excitation energy. The spectrum of a molecule containing these chromophores is complex. This is because the superposition of rotational and vibrational transitions on the electronic transitions gives a combination of overlapping lines. This appears as a continuous absorption band.

Possible *electronic* transitions of □ , □ , and *n* electrons are;



□ □ □ □*□Transitions

An electron in a bonding □ orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, methane (which has only C-H bonds, and can only undergo □ □ □ □*□transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to □ □ □ □*□transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

n□□ □ □* Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of *n*□ □ □ *□transitions. These transitions usually need less energy than □ □ □ □ □*□transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with *n*□ □ □ *□peaks in the UV region is small.

n□□ □ □* and □ □ □ □*□Transitions

Most absorption spectroscopy of organic compounds is based on transitions of *n* or □ electrons to the □* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the □ electrons.

Molar absorbtivities from *n*□ □ □ *□transitions are relatively low, and range from 10 to100 L mol^{-1} cm^{-1} . □ □ □ □ □*□transitions normally give molar absorbtivities between 1000 and 10,000 L mol^{-1} cm^{-1} .

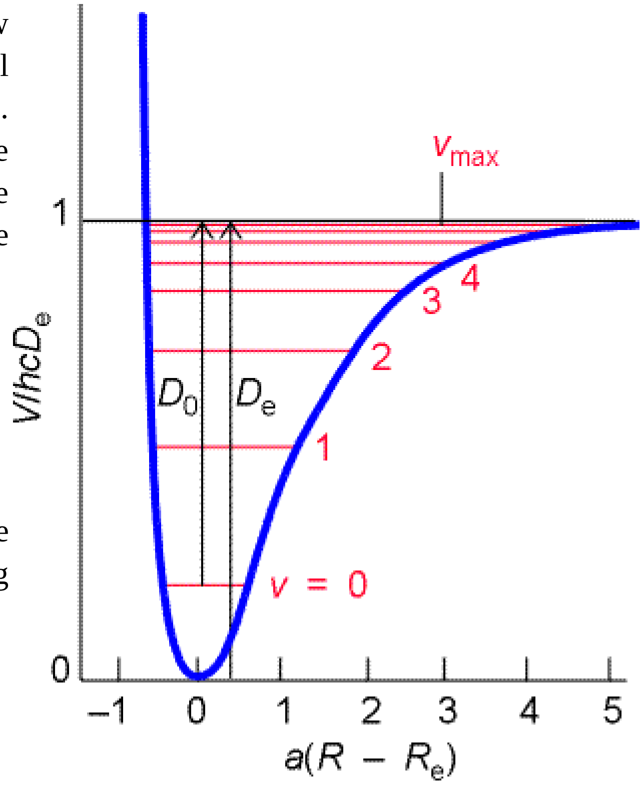
The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from *n*□ □ □ *□transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the *n* orbital. Often (but *not* always), the reverse (i.e. *red shift*) is seen for □ □ □ □ *□transitions. This is caused by attractive polarisation forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences *n*□ □ □ *□ transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

Charge - Transfer Absorption

Many inorganic species show charge-transfer absorption and are called *charge-transfer complexes*. For a complex to demonstrate charge-transfer behaviour, one of its components must have electron donating properties and another component must be able to accept electrons. Absorption of radiation then involves the transfer of an electron from the donor to an orbital associated with the acceptor.

Molar absorbtivities from charge-transfer absorption are large (greater that 10,000 L mol^{-1} cm^{-1}).

26. Write short note on Vibrational and Rotational Transitions of Diatomic Molecules.



High-resolution gas-phase IR spectra show information about the vibrational and rotational behavior of heteronuclear diatomic molecules. Vibrational transitions of HCl and DCl may be modeled by the harmonic oscillator when the bond length is near R_e. In this region, the potential energy can be calculated as:

$$E = \frac{1}{2}k(R - R_e)^2 \quad (1)$$

where *k* is the force constant of the bond. The Schrödinger equation for a particle undergoing harmonic motion can be modified to give an equation to calculate the *allowed* vibrational energy levels:

$$E\ (V) = (V + 1/2)H\square \qquad (2)$$

where h is Planck's constant, $\square$ is the vibrational frequency, and the vibrational quantum number V = 0, 1, 2, ...

Of course, diatomic molecules do not remain stationary as they undergo vibration; they also rotate through space. The rigid rotor model may be used to approximate the rotational contribution to the IR spectrum of a diatomic molecule. For a rigid rotor, the allowed energy levels may be calculated as:

$$E(J) = \frac{h^2}{8\pi^2 I} J(J+1) \qquad (3)$$

where

$$I = \mu r^2, \quad \mu = \frac{m_1 m_2}{(m_1 + m_2)} \quad (4)$$

where J is the rotational quantum number (with integer values 0, 1, 2, ...), h is Planck's constant, and I is the **moment of inertia** for the molecule (calculated as shown using the **reduced mass**, $\square$, and with $r = r_e$). Note that the equation for $E(J)$ is not necessarily in cm^{-1}; you may have to use a conversion factor to get the desired units.

Adding these vibrational and rotational energy terms gives a first approximation of the value of its energy levels. However, we should also include terms which account for **anharmonicity**, **centrifugal distortion (stretching)**, and the interaction between vibration and rotation. An expression for the energy levels for the heteronuclear diatomic molecule in terms of wavenumbers (cm^{-1}) is:

$$G\ (V, J) = \square_e(V + 1/2) - \square_e X_e(V + 1/2)^2 + B_e J(J + 1) - D_e J^2(J + 1)^2 - \square_e(V + 1/2)J(J + 1) \quad (5)$$

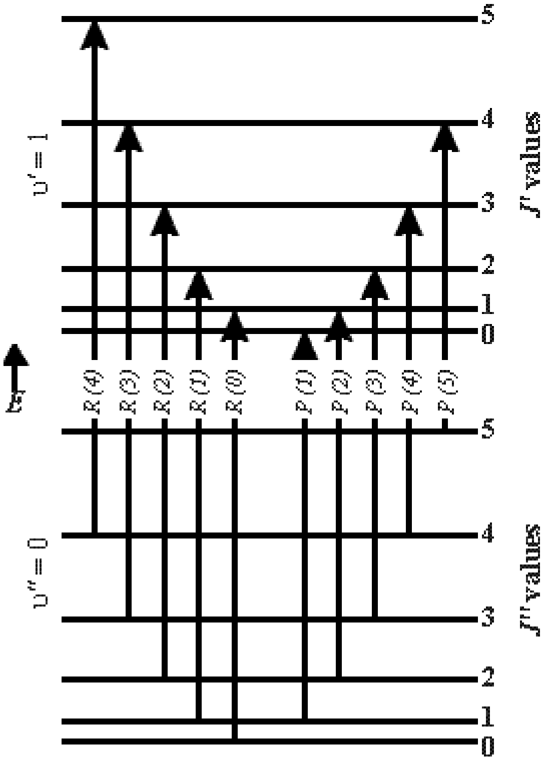
where □$_e$ is the frequency (which we, from now, will express in cm^{-1}, tilda is usually used on the top of □ □ but we will omit it) for the molecule vibrating about the equilibrium bond distance r_e, and

$$B_e = \frac{h}{8\pi^2 I_e c} \quad (6)$$

The difference in energy, and thus the separation between adjacent lines (of the same isotope) in each branch of the IR spectrum, is related to B_e. The first and third terms of the equation for *G* account for the harmonic oscillator and rigid rotor behavior of the diatomic molecule; the second term accounts for anharmonicity (note it contains a constant, x_e); the fourth term takes into account centrifugal stretching, and the last term accounts for the interaction between vibration and rotation. The centrifugal stretching term may be neglected in this experiment since D_e is small, making this term significant only at high *J* values. The last term accounts for the interaction between the vibration and rotation of the molecule; as the molecule vibrates, the moment of inertia changes and the rotation of the molecule is affected. The □$_e$ term is large enough that the final term in the equation for *G* cannot be neglected.

27. Explain the Selection Rules for infrared spectroscopy.

For an harmonic oscillator, the selection rules require that □V = ± 1 and □J = ± 1. That is, when the vibrational transition (represented as V + 1 <-- V) occurs, *J* changes by +1 for the *R* branch and -1 for the *P* branch. Note that □J = 0 is a forbidden transition for the diatomic species we are examining (as having no net spin or orbital angular momentum), so you will not see the *Q* branch corresponding to such a change.



Also, since molecules are not exact harmonic oscillators, I.E. they possess some anharmonic character, weak overtones resulting from □V = ± 2, ± 3, ± 4,... transitions are present, but we will not be concerned with these for the moment. These overtones are important to the blue color of water.

We are most interested in the fundamental transitions from the *J"* levels of the vibrational ground state (V" = 0) to the first excited state *J´* levels corresponding to V' = 1(see figure). The frequency in wavenumbers, □ , may be calculated for the *R* and *P* branches using the following equations:

$$\square_R = \square_o + (2B_e - 3\square_e) + (2B_e - 4\square_e)J'' - \square_e J''^2 \qquad \text{for } J'' = 0, 1, 2, 3...$$

$$\square_P = \square_o - (2B_e - 2\square_e)J'' - \square_e J''^2 \qquad \text{for } J'' = 1, 2, 3... \qquad (7)$$

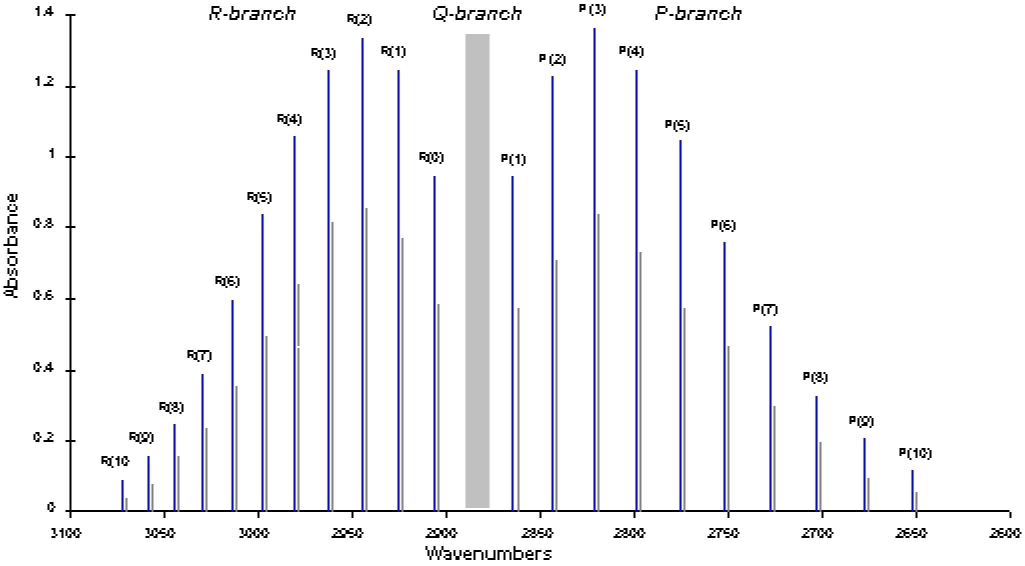
The forbidden transition, $\square_o$, appears at a wavenumber between the *R(0)* and *P(1)* transitions (see figure below; the numbers in parentheses are *J"* values). It is not, however, exactly between the two transitions. Note that the separation between the lines in the *P* branch increases as the *J* values increase while the separation between *R* branch lines decreases. This effect results from the interaction between the vibration and rotation; if there was no interaction, $\square_e$would be zero and the separation between lines would be $2B_e$. The energy of the forbidden transition, $\square_o$, must be calculated using its relation to B_e and $\square_e$ using the equation

$$\square = \square_o + (2B_e - 2\square_e)M - \square_e M^2 \qquad (8)$$

where *m* is an integer and is defined as *m* = *J"* + 1 for the *R* branch and *m* = - J" for the *P* branch. The separation between adjacent lines of the same isotope in the IR spectrum is therefore

$$\square\square(M) = \square\square(M + 1) - \square\square(M) = (2B_e - 3\square_e) - 2\square_e M \qquad (9)$$

The values of B_e and $\square_e$ can be calculated from a plot of □□ (M) versus *m*. Once these two values are determined, $\square_o$ can be calculated using any value of *m* and the Eq.(9).



Isotope Effect

We will discuss the isotope effect with reference to HCl; however, the other gases also exhibit isotope effects and you should analyze them as well.

The most abundant form of HCl is $^{1}H^{35}Cl$. Another isotope of chlorine, ^{37}Cl, has a high natural abundance, however, and the lines for $^{1}H^{37}Cl$ are obvious in a high-resolution spectrum of HCl, right next to the $^{1}H^{35}Cl$ lines. In fact, the isotopic abundance of ^{35}Cl and ^{37}Cl may be calculated from the relative absorbance values in the IR spectrum (since absorbance is proportional to concentration). Though the change of an isotope (e.g., ^{35}Cl to ^{37}Cl) does not effect the equilibrium bond length r_e, or the force constant k for the molecule, varying an isotope does change □, the reduced mass. Since the reduced mass affects the vibrational and rotational behavior or a molecule, the energy of its transitions are affected. For the harmonic oscillator, the vibrational transition occurs at the frequency $□_{\mathrm{HARMONIC}}$, which is given by the equation

$$\nu_{harmonic} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (10)$$

The effect of the reduced mass on $□_{\mathrm{HARMONIC}}$ (disregarding anharmonicity) can be presented in the form of the ratio

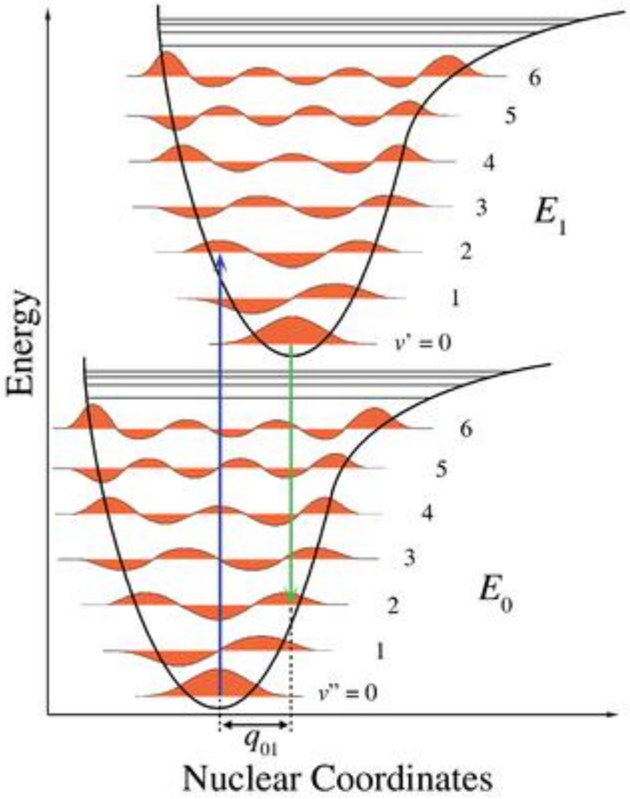
$$\frac{\nu^*_{harmonic}}{\nu_{harmonic}} = \sqrt{\frac{\mu}{\mu^*}} \qquad (11)$$

where the asterisk simply denotes a different isotope (for convenience, use the asterisk to denote the heavier isotope). For the effect of different isotopes on rotation, a similar relationship can be derived as

$$\frac{B^*_e}{B_e} = \frac{\mu}{\mu^*} \qquad (12)$$

Of course, these effects apply to isotopes of hydrogen as well as chlorine.

28. Explain briefly about frank Condon principle?



Using the Franck-Condon principle, we are able to calculate the intensities of transitions between vibrational states of the electronic energy levels. Due to their low mass, electron movement is fast compare with the nuclear movement and we can consider these two movements separately. Particularly, the position of nucleus can be considered as fixed during the electron transition. This means that the electron transition can be drawn as a vertical line on the potential curve diagram. However, after the electron transition took place, the nuclear vibrations move the nucleus toward the position of a new equilibrium distance with respect to the new potential energy curve.In terms of quantum mechanics, the probability of an electron transition is proportional to the squire of the overlap integral between the vibrational wave function $\Psi_{v''}(R)$ and $\Psi_{v'}(R$ before and after the electronic transition.

To treat the problem quantitatively, the complete molecular wave function of the initial and the final state are needed. Fortunately, it is often possible to present this wave function as a product of the electronic wave function Ψ_{el} with depends on the coordinates of all electrons $\mathbf{r}_i$ and the vibrational wave function $\Psi_v(R)$ which is a solution of the Schrödinger equation for nuclei and depend on the inter nuclear distance R. This approach is based on the Born-Oppenheimer approximation which argues with large difference in mass for nuclei and electrons. In the Born-Oppenheimer approximation the probability of a radiative transition is written as

$$W_{k\leftarrow 0} \propto \left|\langle k|\,\mu_Z|0\rangle\right|^2 E_z^2,$$

Where $\langle k|\,\mu_Z|0\rangle$ is the matrix element of the **transition dipole moment**

$$\langle k|\mu_Z|0\rangle \quad = \quad q_{v''v'}\int \Psi_{el_k}{}^*(\mathbf{r}_i)\mu_z\Psi_{el_0}(\mathbf{r}_i)d\mathbf{r}_i$$

$$q_{v''v'} \quad = \quad \int \Psi^*_{v''}(R)\Psi_{v'}(R)dR$$

The integral over the electron coordinates r_i does not dependent on the vibration of nuclei and it is identical for all pairs of v', v''. The integral over R represents overlap of the vibrational wave functions.

The quantities $|q_{v''v'}|^2$ are called **Franck-Condon factors**. No selection rules exist for changes of the vibrational quantum number v. This is because the vibrational wave functions of the initial and final states are in general not orthogonal to each other being the subject of Scrödinger equation with two different potentials $V'(R)$ and $V''(R)$. Apart from that, the **Franck-Condon-principle** allows to calculate the probability of a transition from some vibrational level v' of the initial state to another vibrational level v'' of the final state.