UNIT – I

Electronic Spectroscopy and NMR

Two marks

1. Define Frank condon principle
2. What is dissociation energy
3. Define Born-Oppenheimer Approximation
4. Write about dissociation products
5. What are all the transitions possible in electronic spectroscopy
6. Write the principles of NMR
7. What is chemical shift
8. Write about spin-spin interaction
9. What is coupling constant
10. What is relaxation process

Five Marks

1. Write a note on Born-Oppenheimer Approximation
2. Explain about Frank condon principle
3. Write a short note on Relaxation process
4. Explain about Fortrat diagram
5. Explain about Fourier transform NMR
6. Write about Chemical exchange

Ten Marks

1. Explain briefly about Chemical Shift in NMR
2. Explain about Rotational fine structure of Vibrational transitions
3. Explain about ^{13}C NMR in detail.

Born-Oppenheimer Approximation

The Born-Oppenheimer Approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions and nuclear positions.

This involves the following assumptions:

- The electronic wave function depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
- The nuclear motion (e.g., rotation, vibration) sees a smeared out potential from the speedy electrons.

We know that if a Hamiltonian is separable into two or more terms, then the total eigen functions are products of the individual eigen functions of the separated Hamiltonian terms, and the total eigen values are sums of individual eigen values of the separated Hamiltonian terms.

Consider, for example, a Hamiltonian which is separable into two terms, one involving coordinate q_1 and the other involving coordinate q_2.

$$H = H_1(q_1) + H_2(q_2)$$

With the overall Schrödinger equation being

$$H\psi(q_1, q_2) = E\psi(q_1, q_2)$$

If we assume that the total wavefunction can be written in the form $\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$ where $\psi_1(q_1)$ and $\psi_2(q_2)$ are eigen functions of H_1 and H_2 with eigenvalues E_1 and E_2, then

$$
\begin{aligned}
H\psi(q_1, q_2) &= (H_1 + H_2)\psi_1(q_1)\psi_2(q_2) \\
&= H_1\psi_1(q_1)\psi_2(q_2) + H_2\psi_1(q_1)\psi_2(q_2) \\
&= E_1\psi_1(q_1)\psi_2(q_2) + E_2\psi_1(q_1)\psi_2(q_2) \\
&= (E_1 + E_2)\psi_1(q_1)\psi_2(q_2) \\
&= E\psi(q_1, q_2)
\end{aligned}
$$

Thus the eigenfunctions of H are products of the eigenfunctions of H_1 and H_2, and the eigenvalues are the sums of eigenvalues of H_1 and H_2 .

Going back to our original problem, we would start by seeking the eigenfunctions and eigenvalues of this Hamiltonian, which will be given by solution of the time-independent Schrödinger equation

$$[T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R})]\, \Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}).$$

We first invoke the Born-Oppenheimer approximation by recognizing that, in a dynamical sense, there is a strong separation of time scales between the electronic and nuclear motion, since the electrons are lighter than the nuclei by three orders of magnitude. This can be exploited by assuming a quasi-separable ansatz of the form

$$\Psi(\mathbf{x}, \mathbf{R}) = \phi_e(\mathbf{x}, \mathbf{R})\phi_N(\mathbf{R})$$

where $\varphi N(R)$ is a nuclear wave function and $\varphi_e (x,R)$ is an electronic wave function that depends parametrically on the nuclear positions. If we look again at the Hamiltonian, we would notice right away that the term V_eN would prevent us from applying this separation of variables. The Born-Oppenheimer (named for its original inventors, Max Born and Robert Oppenheimer) is based on the fact that nuclei are several thousand times heavier than electrons. The proton, itself, is approximately 2000 times more massive than an electron. In a dynamical sense, the electrons can be regarded as particles that follow the nuclear motion adiabatically, meaning that they are ``dragged'' along with the nuclei without requiring a finite relaxation time. This, of course, is an approximation, since there could be non-adiabatic effects that do not allow the electrons to follow in this ``instantaneous'' manner, however, in many systems, the adiabatic separation between electrons and nuclei is an excellent approximation. Another consequence of the mass difference between electrons and nuclei is that the nuclear components of the wave function are spatially more localized than the electronic component of the wave function. In the classical limit, the nuclear are fully localized about single points representing classical point particles.


Franck–Condon principle

The **Franck–Condon principle** is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. The principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.

Electronic transitions are relatively instantaneous compared with the time scale of nuclear motions, therefore if the molecule is to move to a new vibrational level during the electronic transition, this new vibrational level must be instantaneously compatible with the nuclear positions and momenta of the vibrational level of the molecule in the originating electronic state. In the semiclassical picture of vibrations (oscillations) of a simple harmonic oscillator, the necessary conditions can occur at the turning points, where the momentum is zero.

Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of

the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.
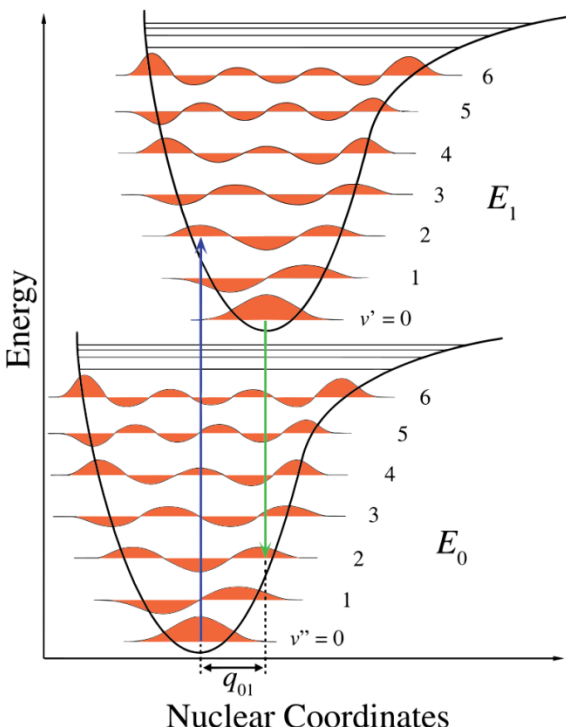
Rotational fine structure of electronic Vibrational Transstion

Electronic transitions are typically observed in the visible and ultraviolet regions, in the wavelength range approximately 200–700 nm ($50,000$–$14,000$ cm^{-1}), whereas fundamental vibrations are observed below about 4000 cm^{-1}.[note 1] When the electronic and vibrational energy changes are so different, vibronic coupling (mixing of electronic and vibrational wave functions) can be neglected and the energy of a vibronic level can be taken as the sum of the electronic and vibrational (and rotational) energies; that is, the Born–Oppenheimer approximation applies.[4] The overall molecular energy depends not only on the electronic state but also on vibrational and rotational quantum numbers, denoted v and J respectively for diatomic molecules. It is conventional to add a double prime (v", J") for levels of the electronic ground state and a single prime (v', J') for electronically excited states.

Each electronic transition may show vibrational coarse structure, and for molecules in the gas phase, rotational fine structure. This is true even when the molecule has a zero dipole moment and therefore has no vibration-rotation infrared spectrum or pure rotational microwave spectrum.[5]

It is necessary to distinguish between absorption and emission spectra. With absorption the molecule starts in the ground electronic state, and usually also in the vibrational

ground state   because at ordinary temperatures the energy necessary for vibrational

excitation is large compared to the average thermal energy. The molecule is excited to

another electronic state and to many possible vibrational states   . With emission, the molecule can start in various populated vibrational states, and finishes in the electronic ground state in one of many populated vibrational levels. The emission spectrum is more complicated than the absorption spectrum of the same molecule because there are more changes in vibrational energy level.

For absorption spectra, the vibrational coarse structure for a given electronic transition forms single *progression*, or series of transitions with a common level, here the lower

level   .There are no selection rules for vibrational quantum numbers, which are zero in the ground vibrational level of the initial electronic ground state, but can take any integer values in the final electronic excited state. The term values $G(\upsilon)$ for a harmonic oscillator are given by

$$G(\upsilon) = \upsilon_{electronic} + \omega_e(\upsilon+1/2)$$

where *v* is a vibrational quantum number, ω_e is the harmonic wavenumber. In the next approximation the term values are given by

$$G(\upsilon) = \upsilon_{electronic} + \omega_e(\upsilon+1/2) - \omega_e x_e(\upsilon+1/2)^2$$

where χ_e is an anharmonicity constant. This is, in effect, a better approximation to the Morse potential near the potential minimum. The spacing between adjacent vibrational lines decreases with increasing quantum number because of anharmonicity in the vibration. Eventually the separation decreases to zero when the molecule photo-dissociates into a continuum of states. The second formula is adequate for small values of the vibrational quantum number. For higher values further anharmonicity terms are needed as the molecule approaches the dissociation limit, at the energy corresponding to the upper (final state) potential curve at infinite internuclear distance.

The intensity of allowed vibronic transitions is governed by the Franck–Condon principle.[7] Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates, that is, when the transition is "vertical" on the energy level diagram. Each line has a finite linewidth, dependent on a variety of factors.[8]

Vibronic spectra of diatomic molecules in the gas phase have been analyzed in detail.[9] Vibrational coarse structure can sometimes be observed in the spectra of molecules in liquid or solid phases and of molecules in solution. Related phenomena including photoelectron spectroscopy, resonance Raman spectroscopy, luminescence,

and fluorescence are not discussed in this article, though they also involve vibronic transitions.
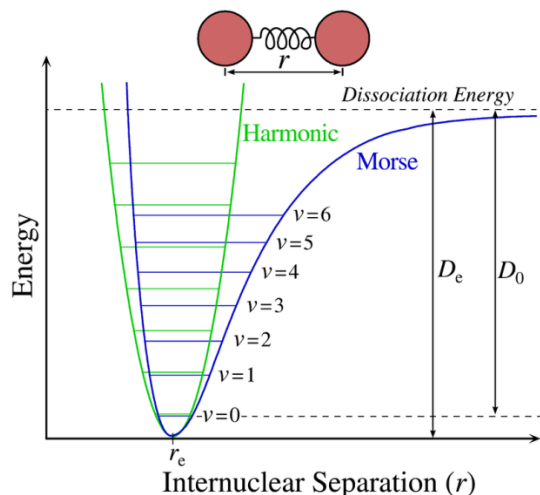
The **Morse potential** (blue) and harmonic oscillator potential (green). The potential at infinite internuclear distance is the dissociation energy for pure vibrational spectra. For vibronic spectra there are two potential curves

NMR

Nuclear magnetic resonance (**NMR**) is a physical phenomenon in which nuclei in a strong constant magnetic field are perturbed by a weak oscillating magnetic field (in the near field[1]) and respond by producing an electromagnetic signal with a frequency characteristic of the magnetic field at the nucleus. This process occurs near resonance, when the oscillation frequency matches the intrinsic frequency of the nuclei, which depends on the strength of the static magnetic field, the chemical environment, and the magnetic properties of the isotope involved; in practical applications with static magnetic fields up to ca. 20 tesla, the frequency is similar to VHF and UHF television broadcasts (60–1000 MHz). NMR results from specific magnetic properties of certain atomic nuclei. Nuclear magnetic resonance spectroscopy is widely used to determine the structure of organic molecules in solution and study molecular physics and crystals as well as non-crystalline materials. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI).

All isotopes that contain an odd number of protons and/or neutrons (see Isotope) have an intrinsic nuclear magnetic moment and angular momentum, in other words a nonzero nuclear spin, while all nuclides with even numbers of both have a total spin of zero. The most commonly used nuclei are ^{1}H and ^{13}C , although isotopes of many other elements can be studied by high-field NMR spectroscopy as well.

A key feature of NMR is that the resonance frequency of a particular sample substance is usually directly proportional to the strength of the applied magnetic field. It is this feature that is exploited in imaging techniques; if a sample is placed in a non-uniform magnetic

field then the resonance frequencies of the sample's nuclei depend on where in the field they are located. Since the resolution of the imaging technique depends on the magnitude of the magnetic field gradient, many efforts are made to develop increased gradient field strength.

The principle of NMR usually involves three sequential steps:

- The alignment (polarization) of the magnetic nuclear spins in an applied, constant magnetic field $\mathbf{B}_0$.
- The perturbation of this alignment of the nuclear spins by a weak oscillating magnetic field, usually referred to as a radio-frequency (RF) pulse. The oscillation frequency required for significant perturbation is dependent upon the static magnetic field ($\mathbf{B}_0$) and the nuclei of observation.
- The detection of the NMR signal during or after the RF pulse, due to the voltage induced in a detection coil by precession of the nuclear spins around $\mathbf{B}_0$. After an RF pulse, precession usually occurs with the nuclei's intrinsic Larmor frequency and, in itself, does not involve transitions between spin states or energy levels.[1]

The two magnetic fields are usually chosen to be perpendicular to each other as this maximizes the NMR signal strength. The frequencies of the time-signal response by the total magnetization (**M**) of the nuclear spins are analyzed in NMR spectroscopy and magnetic resonance imaging. Both use applied magnetic fields ($\mathbf{B}_0$) of great strength, often produced by large currents in superconducting coils, in order to achieve dispersion of response frequencies and of very high homogeneity and stability in order to deliver spectral resolution, the details of which are described by chemical shifts, the Zeeman effect, and Knight shifts (in metals). The information provided by NMR can also be increased using hyperpolarization, and/or using two-dimensional, three-dimensional and higher-dimensional techniques.

NMR phenomena are also utilized in low-field NMR, NMR spectroscopy and MRI in the Earth's magnetic field (referred to as Earth's field NMR), and in several types of magnetometers.

Nuclear spin and magnets

All nucleons, that is neutrons and protons, composing any atomic nucleus, have the intrinsic quantum property of spin, an intrinsic angular momentum analogous to the classical angular momentum of a spinning sphere. The overall spin of the nucleus is determined by the spin quantum number S. If the numbers of both the protons and neutrons in a given nuclide are even then $S = 0$, i.e. there is no overall spin. Then, just as electrons pair up in non degenerate atomic orbitals, so do even numbers of protons or

even numbers of neutrons (both of which are also spin particles and hence fermions), giving zero overall spin.

However, a proton and neutron will have lower energy when their spins are parallel, not anti-parallel. This parallel spin alignment of distinguishable particles does not violate

the Pauli exclusion principle. The lowering of energy for parallel spins has to do with the quark structure of these two nucleons. As a result, the spin ground state for the deuteron (the nucleus of deuterium, the ^{2}H isotope of hydrogen), which has only a proton and a neutron, corresponds to a spin value of **1**, *not of zero*. On the other hand, because of the Pauli exclusion principle, the tritium isotope of hydrogen must have a pair of anti-parallel spin neutrons (of total spin zero for the neutron-spin pair), plus a proton of spin 1/2. Therefore, the tritium total nuclear spin value is again 1/2, just like for the simpler, abundant hydrogen isotope, ^{1}H nucleus (the *proton*). The NMR absorption frequency for tritium is also similar to that of ^{1}H. In many other cases of *non-radioactive* nuclei, the overall spin is also non-zero. For example, the ^{27}Al nucleus has an overall spin value $S = \frac{5}{2}$.

Classically,this corresponds to the proportionality between the angular momentum and the magnetic dipole moment of a spinning charged sphere, both of which are vectors parallel to the rotation axis whose length increases proportional to the spinning frequency. It is the magnetic moment and its interaction with magnetic fields that allows the observation of NMR signal associated with transitions between nuclear spin levels during resonant RF irradiation or caused by Larmor precession of the average magnetic moment after resonant irradiation. Nuclides with even numbers of both protons and neutrons have zero nuclear magnetic dipole moment and hence do not exhibit NMR signal. For instance, ^{18}O is an example of a nuclide that produces no NMR signal, whereas ^{13}C, ^{31}P , ^{35}Cl and ^{37}Cl are nuclides that do exhibit NMR spectra. The last two nuclei have spin $S > 1/2$ and are therefore quadrupolar nuclei.

Values of spin angular momentum

Nuclear spin is an intrinsic angular momentum that is quantized. This means that the magnitude of this angular momentum is quantized (i.e. S can only take on a restricted range of values), and also that the x, y, and z-components of the angular momentum are quantized, being restricted to integer or half-integer multiples of $\hbar$. The integer or half-integer quantum number associated with the spin component along the z-axis or the applied magnetic field is known as the magnetic quantum number, m, and can take values from $+S$ to $-S$, in integer steps. Hence for any given nucleus, there are a total of $2S + 1$ angular momentum states.

Spin energy in a magnetic field
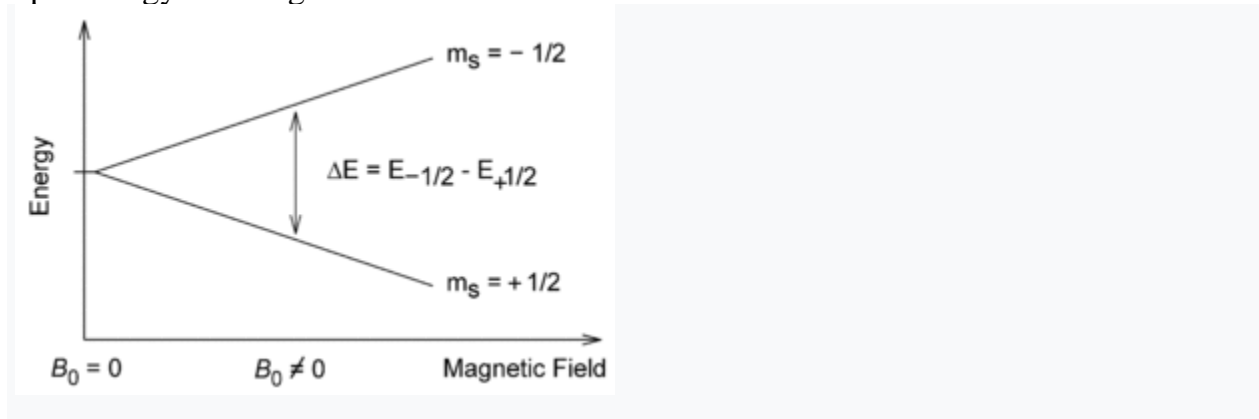
Splitting of nuclei spin energies in an external magnetic fieldConsider nuclei with a spin of one-half, like ^{1}H, ^{13}C or ^{19}F Each nucleus has two linearly independent spin states, with $m = 1/2$ or $m = -1/2$ (also referred to as spin-up and spin-down, or sometimes α and β spin states, respectively) for the z-component of spin. In the absence of a magnetic field, these states are degenerate; that is, they have the same energy. Hence the number of nuclei in these two states will be essentially equal at thermal equilibrium.

Relaxation Process

The process of population relaxation refers to nuclear spins that return to thermodynamic equilibrium in the magnet. This process is also called T_1, "spin-lattice" or "longitudinal magnetic" relaxation, where T_1 refers to the mean time for an individual nucleus to return to its thermal equilibrium state of the spins. After the nuclear spin population has relaxed, it can be probed again, since it is in the initial, equilibrium (mixed) state.

The precessing nuclei can also fall out of alignment with each other and gradually stop producing a signal. This is called T_2 or *transverse relaxation*. Because of the difference in the actual relaxation mechanisms involved (for example, intermolecular versus intramolecular magnetic dipole-dipole interactions), T_1 is usually (except in rare cases) longer than T_2 (that is, slower spin-lattice relaxation, for example because of smaller dipole-dipole interaction effects). In practice, the value of T_2* which is the actually observed decay time of the observed NMR signal, or free induction decay (to $1/e$ of the initial amplitude immediately after the resonant RF pulse), also depends on the static magnetic field inhomogeneity, which is quite significant. (There is also a smaller but significant contribution to the observed FID shortening from the RF inhomogeneity of the resonant pulse).[citation needed] In the corresponding FT-NMR spectrum—meaning the Fourier transform of the free induction decay—the T_2* time is inversely related to the width of the NMR signal in frequency units. Thus, a nucleus with a long T_2 relaxation time gives rise to a very sharp NMR peak in the FT-NMR spectrum for a very homogeneous ("well-shimmed") static magnetic field, whereas nuclei with shorter T_2 values give rise to broad FT-NMR peaks even when the magnet is shimmed well. Both T_1 and T_2 depend on the rate of molecular motions as well as the gyromagnetic ratios of both the resonating and their strongly interacting, next-neighbor nuclei that are not at resonance.

Fourier-transform spectroscopy

Most applications of NMR involve full NMR spectra, that is, the intensity of the NMR signal as a function of frequency. Early attempts to acquire the NMR spectrum more efficiently than simple CW methods involved illuminating the target simultaneously with more than one frequency. A revolution in NMR occurred when short radio-frequency pulses began to be used, with a frequency centered at the middle of the NMR spectrum. In simple terms, a short pulse of a given "carrier" frequency "contains" a range of

frequencies centered about the carrier frequency, with the range of excitation (bandwidth) being inversely proportional to the pulse duration, i.e. the Fourier transform of a short pulse contains contributions from all the frequencies in the neighborhood of the principal frequency.[16] The restricted range of the NMR frequencies made it relatively easy to use short (1 - 100 microsecond) radio frequency pulses to excite the entire NMR spectrum.

Applying such a pulse to a set of nuclear spins simultaneously excites all the single-quantum NMR transitions. In terms of the net magnetization vector, this corresponds to tilting the magnetization vector away from its equilibrium position (aligned along the external magnetic field). The out-of-equilibrium magnetization vector then precesses about the external magnetic field vector at the NMR frequency of the spins. This oscillating magnetization vector induces a voltage in a nearby pickup coil, creating an electrical signal oscillating at the NMR frequency. This signal is known as the free induction decay (FID), and it contains the sum of the NMR responses from all the excited spins. In order to obtain the frequency-domain NMR spectrum (NMR absorption intensity vs. NMR frequency) this time-domain signal (intensity vs. time) must be Fourier transformed. Fortunately, the development of Fourier transform (FT) NMR coincided with the development of digital computers and the digital Fast Fourier Transform. Fourier methods can be applied to many types of spectroscopy. (See the full article on Fourier transform spectroscopy.)

^{13}C NMR Spectroscopy

Carbon-13 (C13) nuclear magnetic resonance (most commonly known as **carbon-13 NMR** or **^{13}C NMR** or sometimes simply referred to as **carbon NMR**) is the application of nuclear magnetic resonance (NMR) spectroscopy to carbon. It is analogous to proton NMR (^{1}H NMR) and allows the identification of carbon atoms in an organic molecule just as proton NMR identifies hydrogen atoms. As such ^{13}C NMR is an important tool in chemical structure elucidation in organic chemistry ^{13}C NMR detects only the ^{13}C isotope of carbon, whose natural abundance is only 1.1%, because the main carbon isotope, ^{13}C, is not detectable by NMR since its nucleus has zero spin.

^{13}C NMR has a number of complications that are not encountered in proton NMR. ^{13}C NMR is much less sensitive to carbon than ^{1}H NMR is to hydrogen since the major isotope of carbon, the ^{12}C isotope, has a spin quantum number of zero and so is not magnetically active and therefore not detectable by NMR. Only the much less common ^{13}C isotope, present naturally at 1.1% natural abundance, is magnetically active with a spin quantum number of 1/2 (like ^{1}H) and therefore detectable by NMR. Therefore, only the few ^{13}C nuclei present resonate in the magnetic field, although this can be overcome by isotopic enrichment of e.g. protein samples. In addition, the gyromagnetic ratio ($6.728284 \ 10^{7}$ rad T^{-1} s^{-1}) is only 1/4 that of ^{1}H, further reducing the sensitivity. The overall *receptivity* of ^{13}C is about 4 orders of magnitude lower than ^{1}H.

High field magnets with internal bores capable of accepting larger sample tubes (typically 10 mm in diameter for ^{13}C NMR versus 5 mm for ^{1}H NMR), the use of relaxation

reagents,[3] for example Cr(acac)$_3$ (chromium(III) acetylacetonate), and appropriate pulse sequences have reduced the time needed to acquire quantitative spectra and have made quantitative carbon-13 NMR a commonly used technique in many industrial labs. Applications range from quantification of drug purity to determination of the composition of high molecular weight synthetic polymers.

In a typical run on an organic compound, a ^{13}C NMR may require several hours to record the spectrum of a one-milligram sample, compared to 15–30 minutes for ^{1}H NMR, and that spectrum would be of lower quality. The nuclear dipole is weaker, the difference in energy between alpha and beta states is one-quarter that of proton NMR, and the Boltzmann population difference is correspondingly less.

Chemical Shift

In nuclear magnetic resonance (NMR) spectroscopy, the **chemical shift** is the resonant frequency of a nucleus relative to a standard in a magnetic field. Often the position and number of chemical shifts are diagnostic of the structure of a molecule.Chemical shifts are also used to describe signals in other forms of spectroscopy such as photoemission spectroscopy.

Some atomic nuclei possess a magnetic moment (nuclear spin), which gives rise to different energy levels and resonance frequencies in a magnetic field. The total magnetic field experienced by a nucleus includes local magnetic fields induced by currents of electrons in the molecular orbitals (note that electrons have a magnetic moment themselves). The electron distribution of the same type of nucleus (e.g. ^{1}H, ^{13}C, ^{15}N) usually varies according to the local geometry (binding partners, bond lengths, angles between bonds, and so on), and with it the local magnetic field at each nucleus. This is reflected in the spin energy levels (and resonance frequencies). The variations of nuclear magnetic resonance frequencies of the same kind of nucleus, due to variations in the electron distribution, is called the chemical shift. The size of the chemical shift is given with respect to a reference frequency or reference sample (see also chemical shift referencing), usually a molecule with a barely distorted electron distribution.

Spin- Spin Coupling

In addition to chemical shift, NMR spectra allow structural assignments by virtue of spin-spin coupling (and integrated intensities). Because nuclei themselves possess a small magnetic field, they influence each other, changing the energy and hence frequency of nearby nuclei as they resonate—this is known as spin-spin coupling. The most important type in basic NMR is *scalar coupling*. This interaction between two nuclei occurs through chemical bonds, and can typically be seen up to three bonds away (3-J coupling), although it can occasionally be visible over four to five bonds, though these tend to be considerably weaker. The effect of scalar coupling can be understood by examination of a proton which has a signal at 1 ppm. This proton is in a hypothetical molecule where three bonds away exists another proton (in a CH-CH group for instance), the neighbouring group (a magnetic field) causes the signal at 1 ppm to split into two, with one peak being

a few hertz higher than 1 ppm and the other peak being the same number of hertz lower than 1 ppm. These peaks each have half the area of the former **singlet** peak. The magnitude of this splitting (difference in frequency between peaks) is known as the coupling constant. A typical coupling constant value for aliphatic protons would be 7 Hz.

The coupling constant is independent of magnetic field strength because it is caused by the magnetic field of another nucleus, not the spectrometer magnet. Therefore, it is quoted in hertz (frequency) and not ppm (chemical shift).

In another molecule a proton resonates at 2.5 ppm and that proton would also be split into two by the proton at 1 ppm. Because the magnitude of interaction is the same the splitting would have the same coupling constant 7 Hz apart. The spectrum would have two signals, each being a **doublet**. Each doublet will have the same area because both doublets are produced by one proton each.

The two doublets at 1 ppm and 2.5 ppm from the fictional molecule CH-CH are now changed into CH_2-CH:

- The total area of the 1 ppm CH_2 peak will be twice that of the 2.5 ppm CH peak.
- The CH_2 peak will be split into a doublet by the CH peak—with one peak at 1 ppm + 3.5 Hz and one at 1 ppm - 3.5 Hz (total splitting or coupling constant is 7 Hz).

In consequence the CH peak at 2.5 ppm will be split *twice* by each proton from the CH_2. The first proton will split the peak into two equal intensities and will go from one peak at 2.5 ppm to two peaks, one at 2.5 ppm + 3.5 Hz and the other at 2.5 ppm - 3.5 Hz—each having equal intensities. However these will be split again by the second proton. The frequencies will change accordingly:

- The 2.5 ppm **+** 3.5 Hz signal will be split into 2.5 ppm + 7 Hz and 2.5 ppm
- The 2.5 ppm **-** 3.5 Hz signal will be split into 2.5 ppm and 2.5 ppm - 7 Hz

The net result is not a signal consisting of 4 peaks but three: one signal at 7 Hz above 2.5 ppm, two signals occur at 2.5 ppm, and a final one at 7 Hz below 2.5 ppm. The ratio of height between them is 1:2:1. This is known as a **triplet** and is an indicator that the proton is three-bonds from a CH_2 group.

This can be extended to any CH_n group. When the CH_2-CH group is changed to CH_3-CH_2, keeping the chemical shift and coupling constants identical, the following changes are observed:

- The relative areas between the CH_3 and CH_2 subunits will be 3:2.
- The CH_3 is coupled to two protons into a 1:2:1 **triplet** around 1 ppm.
- The CH_2 is coupled to *three* protons.

UNIT – II
ESR and Photoelectron

Two Marks

1. Write the principles of ESR
2. Define Mcconnel equation
3. Write abour g-Values in ESR
4. Give the spectral lines for methyl and naphthalene radicals
5. Give some applications of ESR
6. What is Photoelectron spectroscopy
7. Write the principles of X-ray photoelectron spectroscopy
8. What are the source used in photo electron spectroscopy
9. What is auger electron spectroscopy
10. Give some applications of electron spectroscopy

Five Marks

1. Write a note on Hyper Fine splitting
2. Explain the applications of some simple molecules in ESR
3. Explain about Ultra violet photoelectron spectroscopy
4. Write a note on X-ray photoelectron spectroscopy

Ten Marks

1. Explain in detail about Zero field splitting and Krammer's degeneracy
2. Explain briefly about g-Value in ESR
3. Explain the instrumentation of Photoelectron Spectroscopy
4. Explain about Auger electron Spectroscopy.

Electron paramagnetic resonance

Electron paramagnetic resonance (**EPR**) or **electron spin resonance** (**ESR**) spectroscopy is a method for studying materials with **unpaired electrons**. The basic concepts of EPR are analogous to those of nuclear magnetic resonance (NMR), but it is electron spins that are excited instead of the spins of atomic nuclei. EPR spectroscopy is particularly useful for studying metal complexes or organic radicals.

Origin of an EPR signal

Every electron has a magnetic moment and spin quantum number , with magnetic components or In the presence of an external magnetic field with strength , the electron's

magnetic moment aligns itself either antiparallel or parallel to the field, each alignment having a specific energy due to the Zeeman effect:

$m_s=-1/2$

Energy

$\Delta E=E_{-1/2}-E_{+1/2}$

$m_s=+1/2$

$B_0=0$ $\quad$ $B_0\neq0$ $\quad$ Magnetic field

-
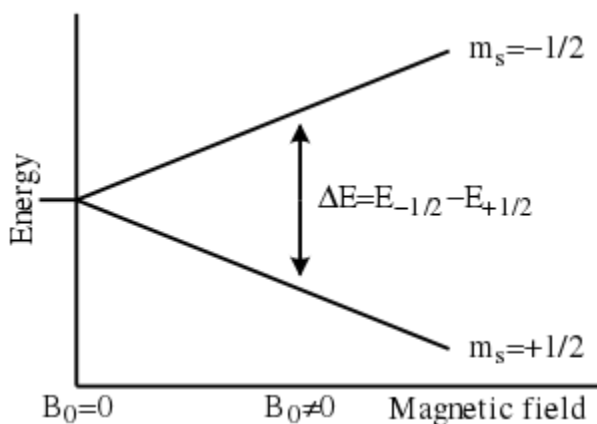
An unpaired electron can move between the two energy levels by either absorbing or emitting a photon of energy such that the resonance condition, , is obeyed. This leads to the fundamental equation of EPR spectroscopy. Experimentally, this equation permits a large combination of frequency and magnetic field values, but the great majority of EPR measurements are made with microwaves in the 9000–10000 MHz (9–10 GHz) region, with fields corresponding to about 3500 G (0.35 T). Furthermore, EPR spectra can be generated by either varying the photon frequency incident on a sample while holding the magnetic field constant or doing the reverse. In practice, it is usually the frequency that is kept fixed. A collection of paramagnetic centers, such as free radicals, is exposed to microwaves at a fixed frequency. By increasing an external magnetic field, the gap between the and energy states is widened until it matches the energy of the microwaves, as represented by the double arrow in the diagram above. At this point the unpaired electrons can move between their two spin states. Since there typically are more electrons in the lower state, due to the Maxwell–Boltzmann distribution (see below), there is a net absorption of energy, and it is this absorption that is monitored and converted into a spectrum. The upper spectrum below is the simulated absorption for a system of free electrons in a varying magnetic field. The lower spectrum is the first derivative of the absorption spectrum. The latter is the most common way to record and publish continuous wave EPR spectra.

Hyperfine coupling

Since the source of an EPR spectrum is a change in an electron's spin state, the EPR spectrum for a radical (S = 1/2 system) would consist of one line. Greater complexity arises because the spin couples with nearby nuclear spins. The magnitude of the coupling is proportional to the magnetic moment of the coupled nuclei and depends on the mechanism of the coupling. Coupling is mediated by two processes, dipolar (through space) and isotropic (through bond).

This coupling introduces additional energy states and, in turn, multi-lined spectra. In such cases, the spacing between the EPR spectral lines indicates the degree of interaction between the unpaired electron and the perturbing nuclei. The hyperfine coupling constant of a nucleus is directly related to the spectral line spacing and, in the simplest cases, is essentially the spacing itself.

Two common mechanisms by which electrons and nuclei interact are the Fermi contact interaction and by dipolar interaction. The former applies largely to the case of isotropic interactions (independent of sample orientation in a magnetic field) and the latter to the case of anisotropic interactions (spectra dependent on sample orientation in a magnetic field). Spin polarization is a third mechanism for interactions between an unpaired electron and a nuclear spin, being especially important for electron organic radicals, such as the benzene radical anion. The symbols "a" or "A" are used for isotropic hyperfine coupling constants, while "B" is usually employed for anisotropic hyperfine coupling constants.

In many cases, the isotropic hyperfine splitting pattern for a radical freely tumbling in a solution (isotropic system) can be predicted.

Application

EPR/ESR spectroscopy is used in various branches of science, such as biology, chemistry and physics, for the detection and identification of free radicals in the solid, liquid, or gaseous state,[8] and in paramagnetic centers such as F-centers. EPR is a sensitive, specific method for studying both radicals formed in chemical reactions and the reactions themselves. For example, when ice (solid H_2O) is decomposed by exposure to high-energy radiation, radicals such as H, OH, and HO_2 are produced. Such radicals can be identified and studied by EPR. Organic and inorganic radicals can be detected in electrochemical systems and in materials exposed to UV light. In many cases, the reactions to make the radicals and the subsequent reactions of the radicals are of interest, while in other cases EPR is used to provide information on a radical's geometry and the orbital of the unpaired electron. EPR/ESR spectroscopy is also used in geology and archaeology as a dating tool. It can be applied to a wide range of materials such as carbonates, sulfates, phosphates, silica or other silicates.

Electron paramagnetic resonance (EPR) has proven itself as a useful tool in homogeneous catalysis research for characterization of paramagnetic complexes and reactive intermediates.EPR spectroscopy is a particularly useful tool to investigate their electronic structures, which is fundamental to understand their reactivity.

Medical and biological applications of EPR also exist. Although radicals are very reactive, and so do not normally occur in high concentrations in biology, special reagents have been developed to spin-label molecules of interest. These reagents are particularly useful in biological systems. Specially-designed nonreactive radical molecules can attach to specific sites in a biological cell, and EPR spectra can then give information on the environment of these so-called spin labels or spin probes. Spin-labeled fatty acids have

been extensively used to study dynamic organisation of lipids in biological membranes, lipid-protein interactions and temperature of transition of gel to liquid crystalline phases.

A type of dosimetry system has been designed for reference standards and routine use in medicine, based on EPR signals of radicals from irradiated polycrystalline α-alanine (the alanine deamination radical, the hydrogen abstraction radical, and the $(CO-(OH))=C(CH3)NH+2$ radical). This method is suitable for measuring gamma and X-rays, electrons, protons, and high-linear energy transfer (LET) radiation of doses in the 1 Gy to 100 kGy range.

EPR/ESR spectroscopy can be applied only to systems in which the balance between radical decay and radical formation keeps the free radicals concentration above the detection limit of the spectrometer used. This can be a particularly severe problem in studying reactions in liquids. An alternative approach is to slow down reactions by studying samples held at cryogenic temperatures, such as 77 K (liquid nitrogen) or 4.2 K (liquid helium). An example of this work is the study of radical reactions in single crystals of amino acids exposed to x-rays, work that sometimes leads to activation energies and rate constants for radical reactions.

The study of radiation-induced free radicals in biological substances (for cancer research) poses the additional problem that tissue contains water, and water (due to its electric dipole moment) has a strong absorption band in the microwave region used in EPR spectrometers.

EPR/ESR also has been used by archaeologists for the dating of teeth. Radiation damage over long periods of time creates free radicals in tooth enamel, which can then be examined by EPR and, after proper calibration, dated. Alternatively, material extracted from the teeth of people during dental procedures can be used to quantify their cumulative exposure to ionizing radiation. People exposed to radiation from the Chernobyl disaster have been examined by this method.

Radiation-sterilized foods have been examined with EPR spectroscopy, the aim being to develop methods to determine whether a particular food sample has been irradiated and to what dose.

EPR can be used to measure microviscosity and micropolarity within drug delivery systems as well as the characterization of colloidal drug carriers.

EPR/ESR spectroscopy has been used to measure properties of crude oil, in particular asphaltene and vanadium content. EPR measurement of asphaltene content is a function of spin density and solvent polarity. Prior work dating to the 1960s has demonstrated the ability to measure vanadium content to sub-ppm levels.

In the field of quantum computing, pulsed EPR is used to control the state of electron spin qubits in materials such as diamond, silicon and gallium arsenide.

Zero field splitting

Zero field splitting (**ZFS**) describes various interactions of the energy levels of a molecule or ion resulting from the presence of more than one unpaired electron. In quantum mechanics, an energy level is called degenerate if it corresponds to two or more different measurable states of a quantum system. In the presence of a magnetic field, the Zeeman effect is well known to split degenerate states. In quantum mechanics terminology, the degeneracy is said to be "lifted" by the presence of the magnetic field. In the presence of more than one unpaired electron, the electrons mutually interact to give rise to two or more energy states. Zero field splitting refers to this lifting of degeneracy even in the absence of a magnetic field. ZFS is responsible for many effects related to the magnetic properties of materials, as manifested in their electron spin resonance spectra and magnetism.[1]

The classic case for ZFS is the spin triplet, i.e., the S=1 spin system. In the presence of a magnetic field, the levels with different values of magnetic spin quantum number ($M_S=0,\pm1$) are separated and the Zeeman splitting dictates their separation. In the absence of magnetic field, the 3 levels of the triplet are isoenergetic to the first order. However, when the effects of inter-electron repulsions are considered, the energy of the three sublevels of the triplet can be seen to have separated. This effect is thus an example of ZFS. The degree of separation depends on the symmetry of the system.

photoelectron spectroscopy

Photoemission spectroscopy (**PES**), also known as **photoelectron spectroscopy**,[1] refers to energy measurement of electrons emitted from solids, gases or liquids by the photoelectric effect, in order to determine the binding energies of electrons in the substance. The term refers to various techniques, depending on whether the ionization energy is provided by X-ray photons or ultraviolet photons. Regardless of the incident photon beam, however, all photoelectron spectroscopy revolves around the general theme of surface analysis by measuring the ejected electrons.

The physics behind the PES technique is an application of the photoelectric effect. The sample is exposed to a beam of UV or XUV light inducing photoelectric ionization. The energies of the emitted photoelectrons are characteristic of their original electronic states, and depend also on vibrational state and rotational level. For solids, photoelectrons can escape only from a depth on the order of nanometers, so that it is the surface layer which is analyzed.

Because of the high frequency of the light, and the substantial charge and energy of emitted electrons, photoemission is one of the most sensitive and accurate techniques for measuring the energies and shapes of electronic states and molecular and atomic orbitals. Photoemission is also among the most sensitive methods of detecting substances in trace concentrations, provided the sample is compatible with ultra-high vacuum and the analyte can be distinguished from background.

Typical PES (UPS) instruments use helium gas sources of UV light, with photon energy up to 52 eV (corresponding to wavelength 23.7 nm). The photoelectrons that actually

escaped into the vacuum are collected, slightly retarded, energy resolved, and counted. This results in a spectrum of electron intensity as a function of the measured kinetic energy. Because binding energy values are more readily applied and understood, the kinetic energy values, which are source dependent, are converted into binding energy values, which are source independent. This is achieved by applying Einstein's relation . The term of this equation is the energy of the UV light quanta that are used for photoexcitation. Photoemission spectra are also measured using tunable synchrotron radiation sources.

The binding energies of the measured electrons are characteristic of the chemical structure and molecular bonding of the material. By adding a source monochromator and increasing the energy resolution of the electron analyzer, peaks appear with full width at half maximum (FWHM) less than 5–8 meV.

Photoelectron spectroscopy (PES) is a technique used for determining the ionization potentials of molecules. Underneath the banner of PES are two separate techniques for quantitative and qualitative measurements. They are ultraviolet photoeclectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). XPS is also known under its former name of electron spectroscopy for chemical analysis (ESCA). UPS focuses on inoization of valence electrons while XPS is able to go a step further and ionize core electrons and pry them away.

Photoelectron Instrumentation

The main goal in either UPS or XPS is to gain information about the composition, electronic state, chemical state, binding energy, and more of the surface region of solids. The key point in PES is that a lot of qualitative and quantitative information can be learned about the surface region of solids. Specifics about what can be studied using XPS or UPS will be discussed in detail below in separate sections for each technique following a discussion on instrumentation for PES experiments. The focus here will be on how the instrumentation for PES is constructed and what types of systems are studied using XPS and UPS. The goal is to understand how to go about constructing or diagramming a PES instrument, how to choose an appropriate analyzer for a given system, and when to use either XPS or UPS to study a system.

There are a few basics common to both techniques that must always be present in the instrumental setup.

1. **A radiation source:** The radiation sources used in PES are fixed-energy radiation sources. XPS sources from x-rays while UPS sources from a gas discharge lamp.

2. **An analyzer:** PES analyzers are various types of electron energy analyzers

3. **A high vacuum environment**: PES is rather picky when it comes to keeping the surface of the sample clean and keeping the rest of the environment free of interferences from things like gas molecules. The high vacuum is almost always an ultra high vacuum (UHV) environment.
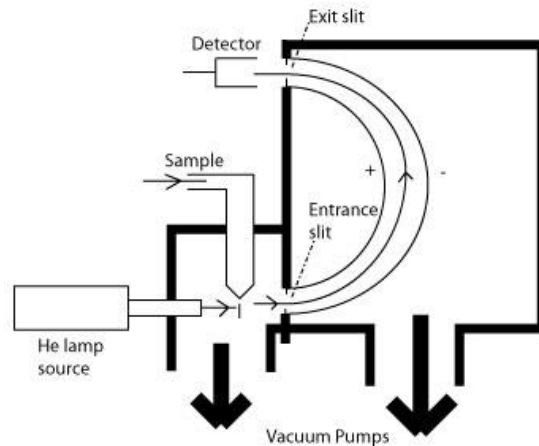
Diagram of a basic, typical PES instrument used in XPS, where the radiation source is an X-ray source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit.

Radiation sources

While many components of instruments used in PES are common to both UPS and XPS, the radiation sources are one area of distinct differentiation. The radiation source for UPS is a gas discharge lamp, with the typical one being an He discharge lamp operating at 58.4 nm which corresponds to 21.2 eV of kinetic energy. XPS has a choice between a monocrhomatic beam of a few microns or an unfocused non-monochromatic beam of a couple centimeters. These beams originate from X-Ray sources of either Mg or Al K-? sources giving off 1486 eV and 1258 eV of kinetic energy respectively. For a more versitile light source, synchrotron radiation sources are also used. Synchrotron radiation is especially useful in studying valence levels as it provides continuous, polarized radiation with high energies of > 350 eV.

The main thing to consider when choosing a radiation source is the kinetic energy involved. The source is what sets the kinetic energy of the photoelectrons, so there needs to not only be enough energy present to cause the ionizations, but there must also be an analyzer capable of measuring the kinetic energy of the released photoelectrons.

In XPS experiments, electron guns can also be used in conjunction with x-rays to eject photoelectrons. There are a couple of advantages and disadvantages to doing this, however. With an electron gun, the electron beam is easily focused and the excitation of photoelectrons can be constantly varied. Unfortunately, the background radiation is increased significantly due to the scattering of falling electrons. Also, a good portion of substances that are of any experimental interest are actually decomposed by heavy electron bombardment such as that coming from an electron gun.

Analyzers

There are two main classes of analyzers well-suited for PES - kinetic energy analyzers and deflection or electrostatic analyzers. Kinetic energy analyzers have a resolving power of $E/\delta EE/\delta E$, which means the higher the kinetic energy of the photoelectrons, the lower the resolution of the spectra. Deflection analyzers are able to separate out photoelectrons through an electric field by forcing electrons to follow different paths according to their velocities, giving a resolving power, $E/\delta EE/\delta E$, that is greater than 1,000.

Since the resolving power of both types of analyzer is $E/\delta EE/\delta E$, the resolution is directly dependent on the kinetic energy of the photoelectrons. The intensity of the spectra produced is also dependent on the kinetic energy. The faster the electrons are moving, the lower the resolution and intensity is. In order to actually get well resolved, useful data other components must be introduced into the instrument.

Adding a system of optics (lenses) to a PES instrument helps with this problem immensely. Electron optics are capable of decelerating the photoelectrons through retardation of the electric field. The energy the photoelectrons decelerate to is known as the "pass energy." This has the benefit of significantly raising the resolution, however this does, unfortunately, lower the sensitivity. Optics are also capable of accelerating the electrons as well. The design of any lens system greatly effects the photoelectron counts. These lenses are also capable of focusing on a small area of a particular sample.

Specific Analyzers

Within the broad picture of two main analyzer classes, there are a variety of specific analyzers in existence that are used in PES. The list below goes over several well-used analyzers, though this list is, by no means, exhaustive. The most common type of analyzer is a hemispherical analyzer, which will be explained in more depth under the spherical deflection analyzer topic.

Plane Mirror Analyzer (PMA)

PMAs, the simplest type of electric analyzer are also known as parallel-plate mirror analyzers. These analyzers are condensers made from two parallel plates with a distance, d, across them. Parabolic trajectories of electrons are obtained due to the constant potential difference, V, between the two plates.

Ultraviolet photoelectron spectroscopy (**UPS**) refers to the measurement of kinetic energy spectra of photoelectrons emitted by molecules which have absorbed ultraviolet photons, in order to determine molecular orbital energies in the valence region.

The UPS measures experimental molecular orbital energies for comparison with theoretical values from quantum chemistry, which was also extensively developed in the 1960s. The photoelectron spectrum of a molecule contains a series of peaks each corresponding to one valence-region molecular orbital energy level. Also, the high resolution allowed the observation of fine structure due to vibrational levels of the

molecular ion, which facilitates the assignment of peaks to bonding, nonbonding or antibonding molecular orbitals.

The method was later extended to the study of solid surfaces where it is usually described as photoemission spectroscopy (PES). It is particularly sensitive to the surface region (to 10 nm depth), due to the short range of the emitted photoelectrons (compared to X-rays). It is therefore used to study adsorbed species and their binding to the surface, as well as their orientation on the surface.[7]

A useful result from characterization of solids by UPS is the determination of the work function of the material. An example of this determination is given by Park et al.[8] Briefly, the full width of the photoelectron spectrum (from the highest kinetic energy/lowest binding energy point to the low kinetic energy cutoff) is measured and subtracted from the photon energy of the exciting radiation, and the difference is the work function. Often, the sample is electrically biased negative to separate the low energy cutoff from the spectrometer response.

X-ray photoelectron spectroscopy (**XPS**) is a surface-sensitive quantitative spectroscopic technique based on the photoelectric effect that can identify the elements that exist within a material (elemental composition) or are covering its surface, as well as their chemical state, and the overall electronic structure and density of the electronic states in the material. XPS is a powerful measurement technique because it not only shows what elements are present, but also what other elements they are bonded to. The technique can be used in line profiling of the elemental composition across the surface, or in depth profiling when paired with ion-beam etching. It is often applied to study chemical processes in the materials in their as-received state or after cleavage, scraping, exposure to heat, reactive gasses or solutions, ultraviolet light, or during ion implantation.

XPS belongs to the family of photoemission spectroscopies in which electron population spectra are obtained by irradiating a material with a beam of X-rays. Material properties are inferred from the measurement of the kinetic energy and the number of the ejected electrons. XPS requires high vacuum (residual gas pressure $p \sim 10^{-6}$ Pa) or ultra-high vacuum ($p < 10^{-7}$ Pa) conditions, although a current area of development is ambient-pressure XPS, in which samples are analyzed at pressures of a few tens of millibar.

When laboratory X-ray sources are used, XPS easily detects all elements except hydrogen and helium. Detection limit is in the parts per thousand range, but parts per million (ppm) are achievable with long collection times and concentration at top surface.

XPS is routinely used to analyze inorganic compounds, metal alloys,[1] semiconductors,[2] polymers, elements, catalysts,[3][4][5][6] glasses, ceramics, paints, papers, inks, woods, plant parts, make-up, teeth, bones, medical implants, bio-materials,[7] coatings,[8] viscous oils, glues, ion-modified materials and many others. Somewhat less routinely XPS is used to analyze the hydrated forms of materials such

as hydrogels and biological samples by freezing them in their hydrated state in an ultrapure environment, and allowing multilayers of ice to sublime away prior to analysis.

Auger electron spectroscopy

Auger electron spectroscopy is a common analytical technique used specifically in the study of surfaces and, more generally, in the area of materials science. Underlying the spectroscopic technique is the Auger effect, as it has come to be called, which is based on the analysis of energetic electrons emitted from an excited atom after a series of internal relaxation events. The Auger effect was discovered independently by both Lise Meitner and Pierre Auger in the 1920s. Though the discovery was made by Meitner and initially reported in the journal *Zeitschrift für Physik* in 1922, Auger is credited with the discovery in most of the scientific community.[1] Until the early 1950s Auger transitions were considered nuisance effects by spectroscopists, not containing much relevant material information, but studied so as to explain anomalies in X-ray spectroscopy data. Since 1953 however, AES has become a practical and straightforward characterization technique for probing chemical and compositional surface environments and has found applications in metallurgy, gas-phase chemistry, and throughout the microelectronics industry.

There are a number of electron microscopes that have been specifically designed for use in Auger spectroscopy; these are termed scanning Auger microscopes (SAMs) and can produce high resolution, spatially resolved chemical images.[1][3][5][7][12] SAM images are obtained by stepping a focused electron beam across a sample surface and measuring the intensity of the Auger peak above the background of scattered electrons. The intensity map is correlated to a gray scale on a monitor with whiter areas corresponding to higher element concentration. In addition, sputtering is sometimes used with Auger spectroscopy to perform depth profiling experiments. Sputtering removes thin outer layers of a surface so that AES can be used to determine the underlying composition.[3][4][5][6] Depth profiles are shown as either Auger peak height vs. sputter time or atomic concentration vs. depth. Precise depth milling through sputtering has made profiling an invaluable technique for chemical analysis of nanostructured materials and thin films. AES is also used extensively as an evaluation tool on and off fab lines in the microelectronics industry, while the versatility and sensitivity of the Auger process makes it a standard analytical tool in research labs.[13][14][15][16] Theoretically, Auger spectra can also be utilized to distinguish between protonation states. When a molecule is protonated or deprotonated, the geometry and electronic structure is changed, and AES spectra reflect this. In general, as a molecule becomes more protonated, the ionization potentials increase and the kinetic energy of the emitted outer shell electrons decreases.[17]

Despite the advantages of high spatial resolution and precise chemical sensitivity attributed to AES, there are several factors that can limit the applicability of this technique, especially when evaluating solid specimens. One of the most common limitations encountered with Auger spectroscopy are charging effects in non-conducting samples.[2][3] Charging results when the number of secondary electrons leaving the sample is different from the number of incident electrons, giving rise to a net positive or

negative electric charge at the surface. Both positive and negative surface charges severely alter the yield of electrons emitted from the sample and hence distort the measured Auger peaks. To complicate matters, neutralization methods employed in other surface analysis techniques, such as secondary ion mass spectrometry (SIMS), are not applicable to AES, as these methods usually involve surface bombardment with either electrons or ions (i.e. flood gun). Several processes have been developed to combat the issue of charging, though none of them is ideal and still make quantification of AES data difficult.[3][6] One such technique involves depositing conductive pads near the analysis area to minimize regional charging. However, this type of approach limits SAM applications as well as the amount of sample material available for probing. A related technique involves thinning or "dimpling" a non-conductive layer with Ar^+ ions and then mounting the sample to a conductive backing prior to AES.[18][19] This method has been debated, with claims that the thinning process leaves elemental artifacts on a surface and/or creates damaged layers that distort bonding and promote chemical mixing in the sample. As a result, the compositional AES data is considered suspect. The most common setup to minimize charging effects includes use of a glancing angle (~10°) electron beam and a carefully tuned bombarding energy (between 1.5 keV and 3 keV). Control of both the angle and energy can subtly alter the number of emitted electrons vis-à-vis the incident electrons and thereby reduce or altogether eliminate sample charging.[2][5][6]

In addition to charging effects, AES data can be obscured by the presence of characteristic energy losses in a sample and higher order atomic ionization events. Electrons ejected from a solid will generally undergo multiple scattering events and lose energy in the form of collective electron density oscillations called plasmons.[2][7] If plasmon losses have energies near that of an Auger peak, the less intense Auger process may become dwarfed by the plasmon peak. As Auger spectra are normally weak and spread over many eV of energy, they are difficult to extract from the background and in the presence of plasmon losses; deconvolution of the two peaks becomes extremely difficult. For such spectra, additional analysis through chemical sensitive surface techniques like x-ray photoelectron spectroscopy (XPS) is often required to disentangle the peaks.[2] Sometimes an Auger spectrum can also exhibit "satellite" peaks at well-defined off-set energies from the parent peak. Origin of the satellites is usually attributed to multiple ionization events in an atom or ionization cascades in which a series of electrons is emitted as relaxation occurs for core holes of multiple levels.[2][3] The presence of satellites can distort the true Auger peak and/or small peak shift information due to chemical bonding at the surface. Several studies have been undertaken to further quantify satellite peaks.[20]

Despite these sometimes substantial drawbacks, Auger electron spectroscopy is a widely used surface analysis technique that has been successfully applied to many diverse fields ranging from gas phase chemistry to nanostructure characterization. Very new class of high-resolving electrostatic energy analyzers recently developed – the face-field analyzers (FFA)[21] can be used for remote electron spectroscopy of distant surfaces or surfaces with large roughness or even with deep dimples. These instruments are designed

as if to be specifically used in combined scanning electron microscopes (SEMs). "FFA" in principle have no perceptible end-fields, which usually distort focusing in most of analysers known, for example, well known CMA.

Sensitivity, quantitative detail, and ease of use have brought AES from an obscure nuisance effect to a functional and practical characterization technique in just over fifty years. With applications both in the research laboratory and industrial settings, AES will continue to be a cornerstone of surface-sensitive electron-based spectroscopies.

UNIT – III
Microwave Spectroscopy

Two marks

11. Define Electromagnetic radiation
12. Write the selection rule for rotational spectroscopy
13. What are the condition of microwave spectroscopy
14. Define Stark effect
15. What is meant by Doppler effect
16. Define Hersenberg uncertainity principle
17. Which type of molecule doesn't show rotational spectrum and why?
18. Define isotopic effect
19. What is meant by prolate and oblate symmetric top molecule
20. Write down the selection rule for symmetry and asymmetric top molecules
21. Write the three type of moment of inertia

Five Marks

1. Write the interaction between electromagnetic radiations and matter
2. What are the classification of rotating molecules.
3. Explain natural line width
4. Write short note on symmetric top molecules
5. Explain Nuclear spin coupling

Ten Marks

1. Derive the energy of rotating diatomic linear molecules
2. Explain the isotopic mass and inter-nuclear distance from microwave spectral studies.

The electromagnetic spectrum

Electromagnetic radiation, as you may recall from a previous chemistry or physics class, is composed of electrical and magnetic waves which oscillate on perpendicular planes. Visible light is electromagnetic radiation. So are the gamma rays that are emitted by spent nuclear fuel, the x-rays that a doctor uses to visualize your bones, the ultraviolet light that causes a painful sunburn when you forget to apply sun block, the infrared light that the army uses in night-vision goggles, the microwaves that you use to heat up your frozen burritos, and the radio-frequency waves that bring music to anybody who is old-fashioned enough to still listen to FM or AM radio.

Just like ocean waves, electromagnetic waves travel in a defined direction. While the speed of ocean waves can vary, however, the speed of electromagnetic waves – commonly referred to as the speed of light – is essentially a constant, approximately 300 million meters per second. This is true whether we are talking about gamma radiation or visible light. Obviously, there is a big difference between these two types of waves – we are surrounded by the latter for more than half of our time on earth, whereas we hopefully

never become exposed to the former to any significant degree. The different properties of the various types of electromagnetic radiation are due to differences in their wavelengths, and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy*.

λ (wavelength)
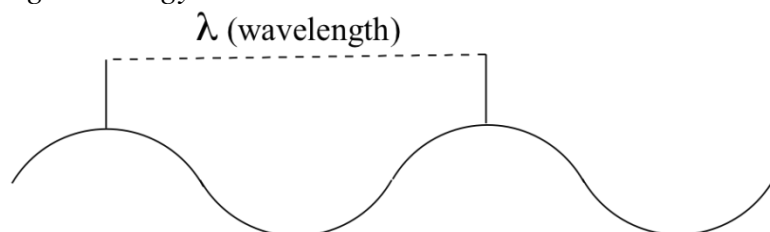
High-energy radiation (such as gamma- and x-rays) is composed of very short waves – as short as 10^{-16} meter from crest to crest. Longer waves are far less energetic, and thus are less dangerous to living things. Visible light waves are in the range of 400 – 700 nm (nanometers, or 10^{-9} m), while radio waves can be several hundred meters in length.

The notion that electromagnetic radiation contains a quantifiable amount of energy can perhaps be better understood if we talk about light as a stream of *particles*, called **photons**, rather than as a wave. (Recall the concept known as 'wave-particle duality': at the quantum level, wave behavior and particle behavior become indistinguishable, and very small particles have an observable 'wavelength'). If we describe light as a stream of photons, the energy of a particular wavelength can be expressed as:

$$E = hc\lambda$$

where E is energy in kJ/mol, λ (the Greek letter *lambda*) is wavelength in meters, *c* is 3.00×10^8 m/s (the speed of light), and *h* is 3.99×10^{-13} kJ·s·mol^{-1}, a number known as **Planck's constant**.

Because electromagnetic radiation travels at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning 'cycles per second', or 'waves per second'. The standard unit for frequency is s^{-1}.

When talking about electromagnetic waves, we can refer either to wavelength or to frequency - the two values are interconverted using the simple expression:

$$\lambda\nu = c$$

where $\mathbf{\nu}$ (the Greek letter '*nu*') is frequency in s^{-1}. Visible red light with a wavelength of 700 nm, for example, has a frequency of 4.29×10^{14} Hz, and an energy of 40.9 kcal per mole of photons. The full range of electromagnetic radiation wavelengths is referred to as the **electromagnetic spectrum**.

The **electromagnetic spectrum** is the range of frequencies (the spectrum) of electromagnetic radiation and their respective wavelengths and photon energies.

The electromagnetic spectrum covers electromagnetic waves with frequencies ranging from below one hertz to above 10^{25} hertz, corresponding to wavelengths from thousands of kilometers down to a fraction of the size of an atomic nucleus. This frequency range is divided into separate bands, and the electromagnetic waves within each frequency band are called by different names; beginning at the low frequency (long wavelength) end of the spectrum these are: radio waves, microwaves, infrared, visible light, ultraviolet, X-rays, and gamma rays at the high-frequency (short wavelength) end. The electromagnetic waves in each of these bands have different characteristics, such as how they are produced, how they interact with matter, and their practical applications. The limit for long wavelengths is the size of the universe itself, while it is thought that the short wavelength limit is in the vicinity of the Planck length.[4] Gamma rays, X-rays, and high ultraviolet are classified as *ionizing radiation* as their photons have enough energy to ionize atoms, causing chemical reactions.

In most of the frequency bands above, a technique called spectroscopy can be used to physically separate waves of different frequencies, producing a spectrum showing the constituent frequencies. Spectroscopy is used to study the interactions of electromagnetic waves with matter.[5] Other technological uses are described under electromagnetic radiation.

Interaction of Electromagnetic Radiation and Matter

It is well known that all matter is comprised of atoms. But subatomically, matter is made up of mostly empty space. For example, consider the hydrogen atom with its one proton, one neutron, and one electron. The diameter of a single proton has been measured to be about 10^{-15} meters. The diameter of a single hydrogen atom has been determined to be 10^{-10} meters, therefore the ratio of the size of a hydrogen atom to the size of the proton is 100,000:1. Consider this in terms of something more easily pictured in your mind. If the nucleus of the atom could be enlarged to the size of a softball (about 10 cm), its electron would be approximately 10 kilometers away. Therefore, when electromagnetic waves pass through a material, they are primarily moving through free space, but may have a chance encounter with the nucleus or an electron of an atom.

Because the encounters of photons with atom particles are by chance, a given photon has a finite probability of passing completely through the medium it is traversing. The probability that a photon will pass completely through a medium depends on numerous factors including the photon's energy and the medium's composition and thickness. The more densely packed a medium's atoms, the more likely the photon will encounter an atomic particle. In other words, the more subatomic particles in a material (higher Z number), the greater the likelihood that interactions will occur Similarly, the more material a photon must cross through, the more likely the chance of an encounter.

When a photon does encounter an atomic particle, it transfers energy to the particle. The energy may be reemitted back the way it came (reflected), scattered in a different direction or transmitted forward into the material. Let us first consider the interaction of visible light. Reflection and transmission of light waves occur because the light waves transfer energy to the electrons of the material and cause them to vibrate. If the material is transparent, then the vibrations of the electrons are passed on to neighboring atoms through the bulk of the material and reemitted on the opposite side of the object. If the material is opaque, then the vibrations of the electrons are not passed from atom to atom through the bulk of the material, but rather the electrons vibrate for short periods of time and then reemit the energy as a reflected light wave. The light may be reemitted from the surface of the material at a different wavelength, thus changing its color.

Microwave Spectroscopy

Selecton rule

For **rotational spectra** the gross **selection rule** is: All molecules that do not possess a permanent dipole moment are **microwave** inactive. This **selection rule** can be rationalized on the basis of the conservation of angular momentum. The photon has an intrinsic angular momentum of one unit.

Stark effect

The **Stark effect** is the shifting and splitting of spectral lines of atoms and molecules due to the presence of an external electric field. It is the electric-field analogue of the Zeeman effect, where a spectral line is split into several components due to the presence of the magnetic field. Although initially coined for the static case, it is also used in the wider context to describe the effect of time-dependent electric fields. In particular, the Stark effect is responsible for the pressure broadening (Stark broadening) of spectral lines by charged particles in plasmas. For most spectral lines, the Stark effect is either linear (proportional to the applied electric field) or quadratic with a high accuracy.

The Stark effect can be observed both for emission and absorption lines. The latter is sometimes called the **inverse Stark effect**, but this term is no longer used in the modern literature.

An electric field pointing from left to right, for example, tends to pull nuclei to the right and electrons to the left. In another way of viewing it, if an electronic state has its electron disproportionately to the left, its energy is lowered, while if it has the electron disproportionately to the right, its energy is raised.

Other things being equal, the effect of the electric field is greater for outer electron shells, because the electron is more distant from the nucleus, so it travels farther left and farther right.

The Stark effect can lead to splitting of degenerate energy levels. For example, in the Bohr model, an electron has the same energy whether it is in the 2s state or any of the 2p states. However, in an electric field, there will be hybrid orbitals (also

called quantum superpositions) of the 2s and 2p states where the electron tends to be to the left, which will acquire a lower energy, and other hybrid orbitals where the electron tends to be to the right, which will acquire a higher energy. Therefore, the formerly degenerate energy levels will split into slightly lower and slightly higher energy levels.

In the presence of a static external electric field the $2J+1$ degeneracy of each rotational state is partly removed, an instance of a Stark effect. For example, in linear molecules each energy level is split into $J+1$ components. The extent of splitting depends on the square of the electric field strength and the square of the dipole moment of the molecule.[30] In principle this provides a means to determine the value of the molecular dipole moment with high precision. Examples include carbonyl sulfide, OCS, with μ = 0.71521 ± 0.00020 Debye. However, because the splitting depends on μ^2, the orientation of the dipole must be deduced from quantum mechanical considerations.[31]

A similar removal of degeneracy will occur when a paramagnetic molecule is placed in a magnetic field, an instance of the Zeeman effect. Most species which can be observed in the gaseous state are diamagnetic . Exceptions are odd-electron molecules such as nitric oxide, NO, nitrogen dioxide, NO_2, some chlorine oxides and the hydroxyl radical. The Zeeman effect has been observed with dioxygen, O_2

Nuclear spin coupling

In atomic nuclei, the spin–orbit interaction is much stronger than for atomic electrons, and is incorporated directly into the nuclear shell model. In addition, unlike atomic–electron term symbols, the lowest energy state is not $L - S$, but rather, $\ell + s$. All nuclear levels whose ℓ value (orbital angular momentum) is greater than zero are thus split in the shell model to create states designated by $\ell + s$ and $\ell - s$. Due to the nature of the shell model, which assumes an average potential rather than a central Coulombic potential, the nucleons that go into the $\ell + s$ and $\ell - s$ nuclear states are considered degenerate within each orbital (e.g. The $2p3/2$ contains four nucleons, all of the same energy. Higher in energy is the $2p1/2$ which contains two equal-energy nucleons).

Symmetric top

For symmetric rotors a quantum number J is associated with the total angular momentum of the molecule. For a given value of J, there is a $2J+1$- fold degeneracy with the quantum number, M taking the values $+J$ ...0 ... $-J$. The third quantum number, K is associated with rotation about the principal rotation axis of the molecule. In the absence of an external electrical field, the rotational energy of a symmetric top is a function of only J and K and, in the rigid rotor approximation, the energy of each rotational state is given by
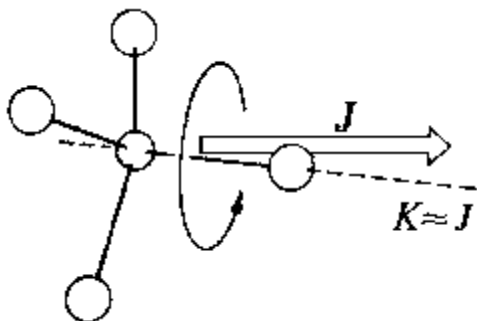
Asymmetric top

The quantum number J refers to the total angular momentum, as before. Since there are three independent moments of inertia, there are two other independent quantum numbers to consider, but the term values for an asymmetric rotor cannot be derived in closed form. They are obtained by individual matrix diagonalization for each J value. Formulae are available for molecules whose shape approximates to that of a symmetric top.[26]

The water molecule is an important example of an asymmetric top. It has an intense pure rotation spectrum in the far infrared region, below about 200 cm^{-1}. For this reason far infrared spectrometers have to be freed of atmospheric water vapour either by purging with a dry gas or by evacuation. The spectrum has been analyzed in detail.[27