

Module 3 : Molecular Spectroscopy

Lecture 12 : Electronic Spectroscopy

Objectives

After studying this lecture, you will be able to

- Qualitatively order the molecular energy levels into electronic, vibrational, rotational and other energy levels.
- Calculate the relative population of these energy levels.
- Identify the regions of the electromagnetic spectrum corresponding to different molecular transitions.
- Calculate the energy differences in various units that are commonly used in molecular spectroscopy.
- Understand the physical basis of selection rules in general and for electronic spectroscopy in particular.
- Identify different parts of an absorption spectrometer.
- Label electronic energy levels using the total angular momentum quantum number.
- Rationalize the multiplet structure of electronic spectra

12.1 Introduction

We have already studied various aspects of atomic and molecular structure in terms of molecular energy levels and charge densities. In addition to electronic energy levels in molecules, there are other energy levels in a molecule such as vibrational and rotational, just to name a few. All these levels are quantized or discrete. The quantization is a consequence of the boundary conditions (such as finiteness, single valuedness, square integrability) on the wave functions. What this means in physical terms is that in molecular vibrations, the molecules undergo oscillatory motion in a small region of space around the minimum energy structure. In rotational motion, molecules look identical after a rotation by 360° with respect to any axis.

We can not see molecular structures with either the naked eye or even by microscopic cameras. We can only study the transitions between the energy levels of molecules resulting from the absorption and emission of light. To infer from the spectroscopic transition data the correct molecular structure is almost like the work of a detective.

Molecular spectroscopy is a vast and growing subject and we shall qualitatively explore some aspects the principles of spectroscopy and of UV-visible spectroscopy in the present lecture. Vibrational and rotational spectroscopy will be taken up in the next lecture; magnetic resonance methods in lecture 14 and some of the remaining methods in lecture 15.

Molecular Energy Levels

A schematic energy level diagram of a polyatomic molecule is shown in Fig. 12.1

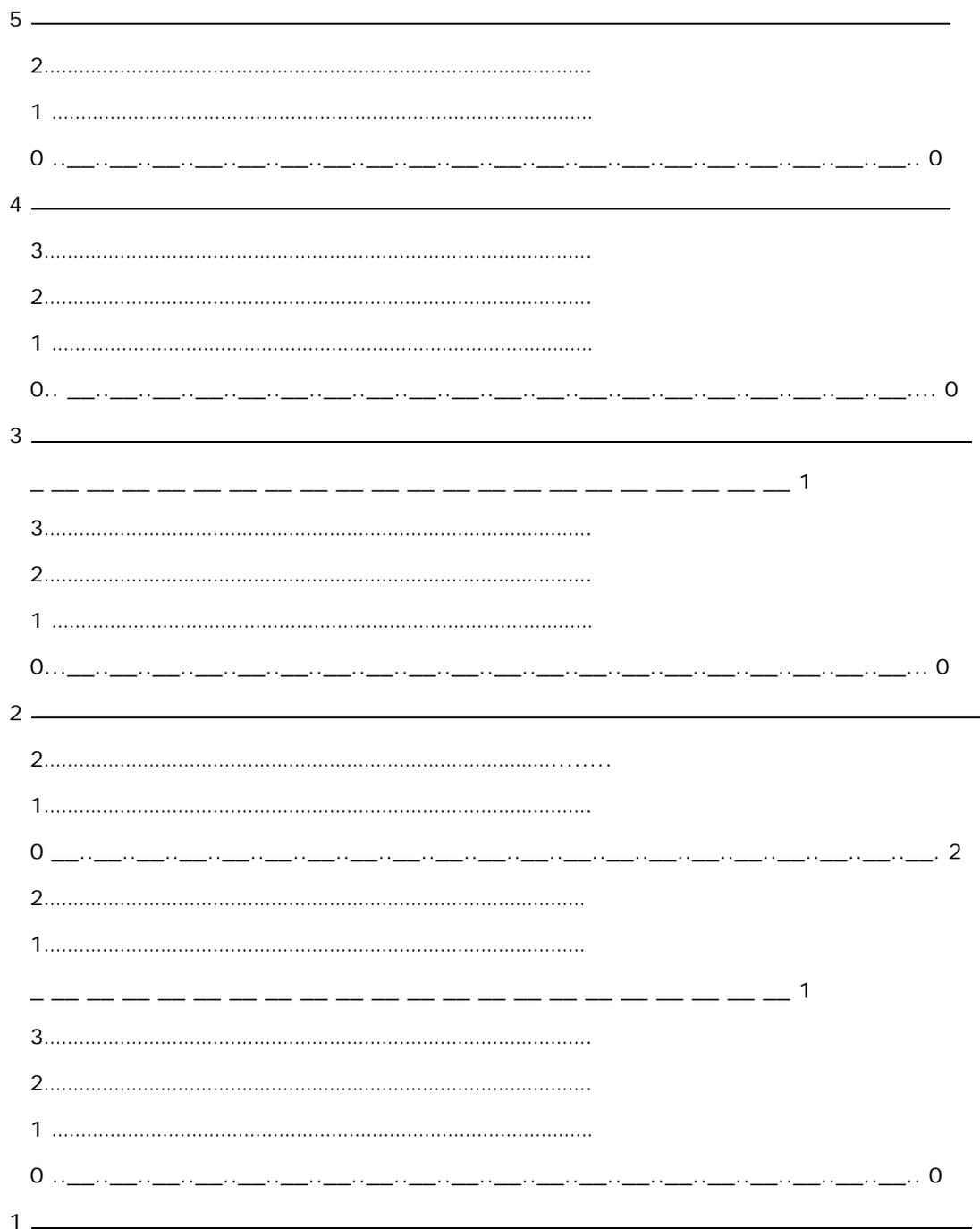


Fig. 12.1 Molecular energy levels. Electronic energy levels are shown by thick lines, vibrational energy levels are shown by dashed lines and rotational energy levels are shown by dotted lines. The quantum numbers corresponding to electronic and rotational levels are shown on the left and the quantum numbers for the vibrational levels are shown on the right.

In Fig. 12.1, the thick lines represent electronic energy levels which are separated from one another by energies in the range of 0.5 to a few electron volts. "Within" (or between two) each electronic energy levels there are several vibrational energy levels and within each vibrational level, there are several rotational energy levels. These energy levels are not equally placed and the spacings between higher levels decrease. The range of energy levels and the region of the electromagnetic radiation that causes transitions between these levels is shown in Table 12.1

Table 12.1 Molecular Energy levels and the Regions of Electromagnetic Radiation

Region of the Spectrum	Frequency Range (Hz)	Wavelength Range	Energy range	Kind of Spectroscopy
X-rays	3×10^{16} to 3×10^{18}	10nm to 100pm	$\sim 10^4$ kJ/mol	X-ray photo-electron Spectroscopy (inner electrons)
Visible and UV	3×10^{14} to 3×10^{16}	1 μ m to 10nm	$\sim 10^2$ kJ/mol	Electronic Spectroscopy
Infrared	3×10^{12} to 3×10^{14}	100 μ m to 1 μ m	~ 10 kJ/mol	Vibrational Spectroscopy
Microwave	3×10^{10} to 3×10^{12}	1cm to 100 μ m	100J/mol	Rotational Spectroscopy
Radio frequency	3×10^6 to 3×10^{10}	10m to 1 cm	0.001 to 10J/mol	Magnetic Resonance Spectroscopy

It is a very convenient approximation to treat the total energy of a molecule as a sum of electronic, vibrational, rotational, nuclear spin, electron spin and other energy levels.

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + \dots \quad (12.1)$$

The above equation follows from the following approximation

$$H_{\text{total}} = H_{\text{electronic}} + H_{\text{vibrational}} + H_{\text{rotational}} + \dots \quad (12.2)$$

On solving the equation (12.2), the following solutions emerge

$$H_{\text{total}} \Psi_{\text{total}} = E_{\text{total}} \Psi_{\text{total}} \quad (12.3a)$$

$$H_{\text{electronic}} \Psi_{\text{electronic}} = E_{\text{electronic}} \Psi_{\text{electronic}} \quad (12.3b)$$

$$H_{\text{vibrational}} \Psi_{\text{vibrational}} = E_{\text{vibrational}} \Psi_{\text{vibrational}} \quad (12.3c)$$

$$H_{\text{rotational}} \Psi_{\text{rotational}} = E_{\text{rotational}} \Psi_{\text{rotational}} \quad (12.3d)$$

For simplicity we will denote rotational vibrational and electronic by subscripts 'r', 'v' and 'e' respectively. The nature of E_e and Ψ_e has already been discussed in the first few lectures by using atomic and molecular orbitals. In the present lecture, we are considering transitions between electronic energy levels. The energy levels have to be calculated by solving the approximate Schrodinger equation (12.3b).

12.3 Selection Rules

Although there are a very large number of energy levels in molecules, transitions are allowed only between specific levels. Several conditions have to met in addition to the primary transition energy requirement, ie,

$$\Delta E = nh\nu \quad (12.4)$$

Normally $n = 1$ and only one photon is absorbed. However, with advances in laser techniques, multiphoton absorption has become possible. In addition to energy conservation in an absorption or emission process, angular momentum has to be conserved during a transition. Photons (particles of light) possess an angular

momentum of \hbar . During an electronic transition, for example, a molecule may get excited from an S state to a P state. In the S state, angular momentum is zero and in the P state, angular momentum is 1 (in units of \hbar). The transition probability $P_{i \rightarrow f}$ from a state ψ_i to a state ψ_f is given by

$$P_{i \rightarrow f} \propto \langle \psi_i | \mu | \psi_f \rangle^2 \quad (12.5)$$

Where μ is the transition dipole operator. Fluctuations in molecular charge densities, dipole moment, polarizability and so on are responsible for this "transition moment" operator.

Another feature that contributes to the intensity of a spectral line is the population of the energy levels. The lower levels are usually more populated than the higher levels and the intensities of absorption lines from lower levels are usually higher. The relative population of energy levels is governed by the Boltzmann distribution at equilibrium.

$$N_{\text{upper}}/N_{\text{lower}} \propto \exp(-\Delta E/k_B T) \quad (12.6)$$

Here, $\Delta E = E_{\text{upper}} - E_{\text{lower}}$, k_B = Boltzmann constant = 1.38×10^{-16} erg/K and T = absolute temperature. When ΔE is large, the number of molecules in the upper level, N_{upper} is very small.

Most of spectroscopy deals with absorption of light. The amount of light absorbed depends on the path length l of the sample (ie the linear extent through which the light travels through the sample), the concentration of the absorbing molecules, c , contained in the sample and the molar absorption coefficient ϵ . The Beer-Lambert law which relates the absorbed intensity of light, I , to the incident intensity I_0 is given by

$$I/I_0 = 10^{-\epsilon c l} \quad (12.7)$$

The quantity I/I_0 is called transmittance. This law is very useful in determining unknown concentrations of molecules in samples when ϵ is already determined by previous experiments. A block diagram of an absorption spectrometer is shown in Fig. 12.2.

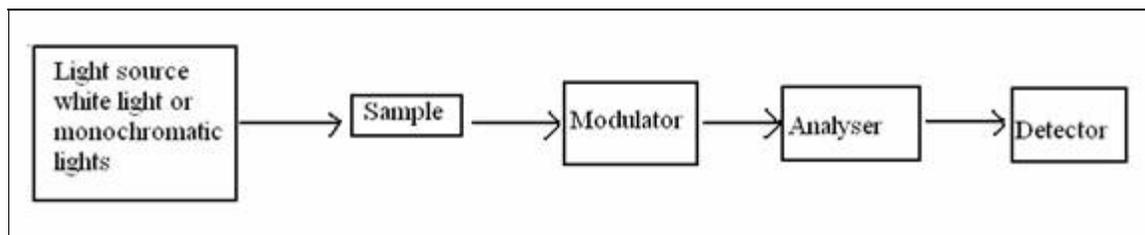


Fig. 12.2 Block diagram of an absorption spectrometer

The modulator is a device that interrupts the radiation several times in a second and converts the signal to an alternating current which is then used for recording. This is useful for amplification of signals and also to reduce the noise levels in the spectrum.

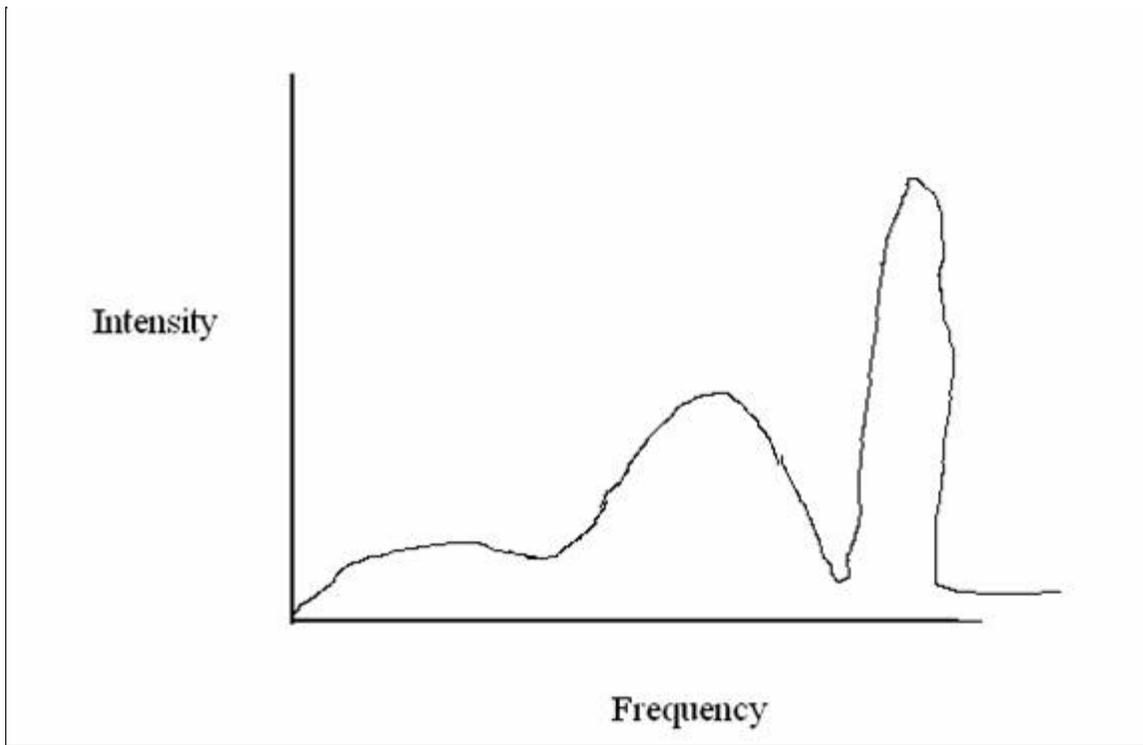


Fig. 12.3 A typical absorption spectrum

Three absorption regions are shown. The one at high frequency is very sharp, while the other two are broad. The width of spectral lines is governed by the uncertainty principle.

$$\Delta E \cdot \Delta t \geq \hbar/2 \quad (12.8)$$

where ΔE is the uncertainty in energy of a state and Δt is the duration in which the state exists.

12.4 Electronic Spectroscopy of Atoms

For hydrogen atom, the selection rules (the rules that govern whether a transition is allowed or not) are

$\Delta n = \text{any integer}$

$$\Delta l = \pm 1 \quad (12.9)$$

The consequences of these conditions are that all transitions from $1s \rightarrow np$ ($n \geq 2$) are allowed. Similarly $2p \rightarrow 3s$, $2p \rightarrow 3d$, $2p \rightarrow 1s$, $3s \rightarrow 4p$, are all allowed transitions. In Equation (12.9), n is the principal quantum number. The well known Lyman series arises from the transitions from the $n = 1$ state to $n' = 2, 3, 4, 5, \dots$. The Balmer series arise from the transitions from the $n = 2$ state to $n' = 3, 4, 5, \dots$. The other series named after Paschen ($n = 3$), Brackett ($n = 4$) and Pfund ($n = 5$) can be readily rationalized. The formula for ΔE is the well known Bohr's formula.

$$\Delta E = R \left\{ \frac{1}{n^2} - \frac{1}{(n')^2} \right\} \quad (12.10)$$

Where n is the initial quantum number and n' , is the number or state resulting from the absorption of radiation. The Rydberg constant $R = 109677.581 \text{ cm}^{-1}$

We have already studied that for each angular momentum L , there are $(2l + 1)$ values of m_l . The values of m_l correspond to the projection of the angular momentum vector L in different directions. In the same manner, the spin angular momentum vector \mathbf{s} can also be projected in $(2s + 1) = 2$ directions. The projections are pictorially shown in Fig. 12.4.

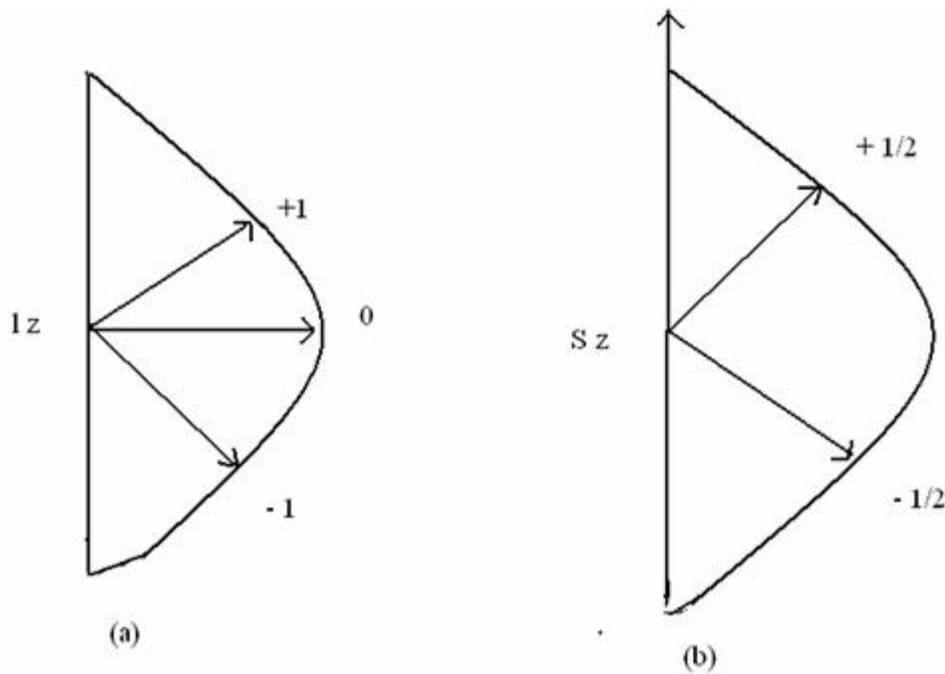


Fig. 12.4 Projections of L and S along the z – axis. The L_z values of 1, 0, -1 are shown in (a) and $s_z = \frac{1}{2}$ and $-\frac{1}{2}$ are shown in (b).

The magnitude of orbital angular momentum L is given by $\sqrt{[l(l + 1)]} \hbar$, where $\hbar = h/2\pi$.

Due to the interaction of these two angular momenta, additional states result and the spectral lines get split into doublets and multiples. New selection rules have to be written in terms of the total angular momentum quantum number J which is defined as

$$J = L + S \quad (12.11)$$

The addition of these angular momenta are governed by special vector addition rules. The values of J and L + S are L – S. For each value of J (with a corresponding magnitude of angular momentum = $\sqrt{[j(j + 1)]} \hbar$) there are $2j + 1$ projections similar to the ones in Fig. 12.4. The new selection rules are

$$\Delta n = \text{any integer} \quad (12.12)$$

$$\Delta j = 0, \pm 1$$

$$\Delta l = \pm 1$$

With the introduction of the total angular momentum, a state is associated with a term symbol.

$$(2s + 1)_L J \quad (12.13)$$

Where $(2s + 1)$ is the spin multiplicity, L = magnitude of orbital angular momentum and J is the total angular momentum. With the new selection rules, the earlier S → P transition which was a single line, now gets split into two lines as follows

$${}^2S_{1/2} \rightarrow {}^2P_{1/2} \quad (\Delta j = 0)$$

$${}^2S_{1/2} \rightarrow {}^2P_{3/2} \quad (\Delta j = +1) \quad (12.14)$$

This splitting of lines is called the fine structure of spectral lines.

In the case of many electron atoms, the degeneracy of 2s and 2p and 3s, 3p and 3d which was present in the H – atom, ceases to exist and the orbital energies are ordered as

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d \quad (12.15)$$

The filling up on electrons in atoms is done by using the Pauli's exclusion principle and the Hund's rule.

According to Hund's rules, states with higher multiplicity are favored, i.e., electrons occupy degenerate orbitals in such a way as to keep their spins parallel.

The spectra of He^+ , Be^+ , B^{2+} which have single electron outside a closed shell show spectra similar to hydrogen. They are referred to as 'hydrogen-like spectra'. In Lithium, the $^2S_{1/2} \rightarrow n^2P_{1/2, 3/2}$ part of the spectrum is similar to hydrogen, but the lines arising from the 2p states form compound doublets as shown below

$$2 \ ^2P_{1/2, 3/2} \rightarrow n \ ^2S_{1/2} \quad (12.16a)$$

$$2 \ ^2P_{1/2, 3/2} \rightarrow n \ ^2D_{3/2, 5/2} \quad (12.16b)$$

When the ground state of an atom has more than one unpaired electron as in the case of carbon, the spectra show a lot of complexity in their structure.

12.5 Electronic spectra of molecules

We have already studied the energy level diagrams of diatomics in earlier lectures. It was pointed out in the beginning of this lecture that $\Delta E_{\text{electronic}} \approx 10^3 \Delta E_{\text{vibrational}} \approx 10^6 \Delta E_{\text{rotational}}$. Although the electronic transition energies are much larger than vibrational and rotational energies, the vibrational "fine" structure is often seen in electronic spectra. We want to summarise the main features of molecular electronic spectroscopy here.

Let us consider the electronic spectrum of molecular hydrogen. Since the molecule has an axis of symmetry (which is the molecular axis; if we rotate the molecule by any angle with respect to this axis, the new molecular orientation or configuration is indistinguishable from the earlier one), the axial component of angular momentum plays an important role. Denoting this by λ , the values that λ can take are 0 (denoted by symbol σ), 1(π), 2(δ), 3(ϕ), and other positive integer values. States with $\lambda > 0$ are doubly degenerate because the projection of the angular momentum on the molecular axis can be positive or negative. The angular momenta of two or more electrons can be added by rules similar to the rules for adding L and S.

In H_2 , the ground state is $(1s\sigma_g)^2 \ ^1\Sigma_g^+$. The meaning of the symbol is that there are two electrons (superscript 2) occupying a σ orbital (the orbital having cylindrical symmetry) formed by the overlap of two 1s orbitals. The subscript g refers to "gerade", which means that the wavefunction (the bonding MO in the present case) is symmetric with respect to the center of symmetry of the molecule. $1s\sigma$ orbital is gerade while $1s\sigma^*$ is ungerade, denoted by subscript u. In $^1\Sigma_g^+$, the + sign refers to symmetry with respect to the reflection across a molecular plane and Σ refers to the total angular momentum of orbital part plus spin part of $\frac{1}{2} + (-\frac{1}{2}) = 0$ for the two electrons.

There are a large number of empty orbitals in H_2 into which the excited electron can be placed.

The three possible excited states of H_2 are

$(1s\sigma_g \ 2s\sigma_g) \ ^1\Sigma_g^+$, $(1s\sigma_g \ 2s\sigma_g) \ ^1\Sigma_u^+$ and $(1s\sigma_g \ 2p \ \pi_u) \ ^1\Pi_u$. The quantities in parenthesis refer to the orbital contributions. In the first case, the total axial angular momentum is zero since $\lambda_1 = \lambda_2$ (the axial angular momentum of each electron) and both are zero. Total angular momentum $\Lambda = \lambda_1 + \lambda_2 = 0$, the total spin $S = 0$ and hence the Σ state. In the third case, $\lambda_2 = 1$ and hence the Π state. The energy ordering of these excited states is found to be

$$^1\Sigma_u^+ < ^1\Pi_u < ^1\Sigma_g^+$$

The selection rules for electronic transitions in diatomics are

$$\Delta\Lambda = 0, \pm 1$$

$$\Delta S = 0$$

$$\Delta\Omega = 0, \pm 1$$

$$\Sigma^+ \leftrightarrow \Sigma^+, \Sigma^- \leftrightarrow \Sigma^-, \Sigma^+ \neq \Sigma^-$$

$$g \leftrightarrow u, g \neq g, u \neq u$$

(12.17)

Using these, it is seen that the first two lines of the electronic energy spectrum in H_2 are $^1\Sigma_g^+ \rightarrow ^1\Sigma_u^+$ and $^1\Sigma_g^+ \rightarrow ^1\Pi_u$. In Eq.(12.17), Λ refers to the total axial angular momentum $\lambda_1 + \lambda_2$, S refers to the total spin $S_1 + S_2$, and Ω refers to the total $\Lambda + S$.

As we go to polyatomics, a simpler way to approach electronic spectra is to consider electronic excitations from various localized orbitals. On excitation, orbital shapes as well as molecular shapes can change significantly. For example, CO_2 becomes bent and $H-C \equiv C-H$ becomes zig-zag. Among organic groups, common frequencies for excitations of $-C=C-$, $>C=O$, $>C=N-$ bonds have been observed. In these molecules which contain double bonds, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are observed. The $n \rightarrow \pi^*$ transitions resulting from the excitation of a non-bonding electron is weak with a low value of extinction coefficient. The $\sigma \rightarrow \sigma^*$ transitions require a lot of energy and occur in the far ultraviolet region (wavelength 100 nm) of the electromagnetic spectrum. The $n \rightarrow \pi^*$ transitions in conjugated ketones may occur in the visible region (400 to 700 nm). The $n \rightarrow \pi^*$ transitions for $C=O$, $C=C$, $C \equiv C$ and $C=N-$ occur at 166, 170, 170 and 190 nm respectively. The $n \rightarrow \pi^*$ transitions in $C=O$ and $C=N-$ occur at 280 and 300 nm respectively. The extinction coefficients of $n \rightarrow \pi^*$ transitions are in the order of ten to thirty thousand while those for $\pi \rightarrow \pi^*$ are small. On conjugation, the wavelength of transitions increase. For example, $-C=C-C=C$ and $-C=C-C=C-C=C-$ have $\pi \rightarrow \pi^*$ transitions at 220 and 260 nm respectively. Substituted conjugated systems have been studied extensively in the UV – visible region and contributions of substituent groups to the changes in peak positions of $\pi \rightarrow \pi^*$ transitions have been quantified and can be used for structural analysis.

12.6 Photoelectron Spectroscopy (PES)

Each electron is held by the nucleus with a characteristic binding energy. The ionization potential is the least energy required to remove this electron from the atom/molecule when high energy radiation ($h\nu$) is incident on a molecule, electrons are ejected from molecules with a large kinetic energy (KE) which is given by

$$h\nu = \text{binding energy} + \text{Kinetic Energy of ejected electrons}$$

This kinetic energy is not quantized. The KE of ejected electrons is analysed by wing hemispherical plates, filters, electron multipliers and analysers. The plot of the number of electrons against their kinetic energy is converted to a plot of intensity versus binding energy to get the photoelectron spectrum. For hydrogen, we get only one binding energy (13.6 eV). For Li, 58 eV (1s electron) and 5.4 eV (2s electron); for F, 694 eV (1s), 37.9 eV (2s) and 17.4 eV (2p), and more lines with fine structure (corresponding to spin orbit interactions) for higher atoms. Using these methods of X-ray PES (XPES) and ultraviolet PES (UPES), elements in a molecule can be detected by using their "fingerprints" generated in atomic PES. While inner electrons in molecules provide good fingerprints, the outer valence electrons are affected by chemical binding and they bear a "molecular" character rather than an atomic character.

12.7 Problems

- 12.1 What are selection rules? Distinguish between the selection rules of electronic spectra of atoms and diatomic molecules.
- 12.2 Convert the wavelength/energy data given in Table 12.1 into electron volts and cm^{-1} . Use $1 \text{ eV} = 8066 \text{ cm}^{-1}$ and $1 \text{ eV} = 96.6 \text{ kJ/mol}$.
- 12.3 If the life time of an excited state is 10^{-9} s , what is uncertainty in its energy? What is the spread in its frequency or the width of the spectral line?
- 12.4 If $\Delta E = 0.1 \text{ kJ/mol}$ between the ground state and the first excited state, what is the population of this excited state at 300 K if the ground state has 10^{23} molecules?.
- 12.5 What is the reason for the yellow doublet in the spectrum of sodium vapor?
- 12.6 What are the first three transitions in the electronic spectrum of H_2 ?

12.7 The $\text{-C}=\text{C-}$ and the $\text{-C}=\text{O}$ groups have $\pi \rightarrow \pi^*$ transitions at 170 and 166 nm respectively. If both these molecules have adjacent Cl and OCH_3 groups, at what wavelengths do you expect the peaks of the $\pi \rightarrow \pi^*$ transitions? A Cl group shifts the peak by 5 nm and an OCH_3 group by 6 nm.

12.8 Rationalize the differences between absorption spectroscopy and emission spectroscopy.

Recap

In this lecture you have learnt the following

12.8 Summary

In the present lecture, you have been introduced to the general principles of spectroscopy and electronic spectroscopy of atoms and molecules. Molecular energies are quantized and molecular energy levels may be conveniently classified as electronic, vibrational, rotational and other energy levels. While there are "cross" interactions between these levels (electronic and vibrational, vibrational and rotational, and so on), the classification is a great aid in studying different aspects of molecular behaviour. A transition between levels is caused by the absorption of electromagnetic radiation. Transitions between energy levels are governed by selection rules. Selection rules are in turn, governed by conservation of energy and angular momentum in addition to the nature of the initial state, the final state and the process occurring within a molecule that connects the two states.

A block diagram of an absorption spectrometer is described. Electronic spectra of hydrogen like atoms are well described by the Bohr's model. Interaction between electron spin and electron angular momenta brings about new levels and doublets and multiplets appear in electronic spectra. For diatomic molecules, an additional quantum number, corresponding to the angular momentum along the internuclear axis is defined and used in selection rules. Term symbols for characterizing the states involved in molecular spectra are briefly outlined. In complex molecules, associating electronic transitions to specific groups such as the ethylenic double bond or the carbonyl group allows one to use electronic spectra for quantitative and qualitative analysis. Photoelectron spectroscopy described towards the end of the lecture allows one to measure the binding energies of different electrons in a molecule and use the atomic binding energy data to characterize molecules as well as surfaces.