ELECTRONIC SPECTROSCOPY AND RAMAN SPECTROSCOPY STUDY MATERIAL

I. ELECTRONIC SPECTROSCOPY

Potential Energy Curves (Diatomic Molecules)

The potential energy of a diatomic molecule is often represented as a function of the internuclear distance (R). These curves illustrate the relationship between the potential energy of the molecule and the distance between the nuclei. Key features include:

- **Equilibrium Bond Distance (R_e):** The internuclear distance at which the potential energy is at a minimum, representing the most stable configuration.
- **Dissociation Limit:** The energy level corresponding to the dissociation of the molecule into two free atoms.
- **Vibrational Energy Levels:** Quantized energy levels superimposed on the potential energy curve, indicating the molecule's vibrational states.

Frank-Condon Principle

This principle governs the intensity of electronic transitions in molecules. It states that electronic transitions are much faster than nuclear motion. Therefore, during an electronic transition, the nuclei remain in their initial positions. This means transitions occur vertically on a potential energy diagram.

- Transitions are most probable between states where the internuclear distance and the shape of the potential energy curves are most similar.
- This explains why some vibrational levels within an electronic transition are more intensely populated than others.

Vibrational Structure of Electronic Spectra

Electronic transitions often lead to a spectrum consisting of multiple lines, corresponding to transitions between different vibrational levels of the upper and lower electronic states. The intensity distribution among these vibronic bands is determined by the Franck-Condon principle.

Franck-Condon Factor

The Franck-Condon factor (FCF) is a quantitative measure of the probability of a vibronic transition. It is the square of the overlap integral between the vibrational wavefunctions of the initial and final electronic states:

FCF = $|\langle \psi_{v'}^{e} | \psi_{v''}^{e} \rangle|^{2}$

where $\psi_{v'}^{e}$ and $\psi_{v''}^{e}$ are the vibrational wavefunctions of the upper and lower electronic states, respectively.

Bond Dissociation and Determination of Dissociation Energy

Electronic spectroscopy can be used to determine bond dissociation energies. By observing the convergence of vibrational energy levels in the upper electronic state towards the dissociation limit, the energy required to break the bond can be found.

- The dissociation energy (D_0) is the energy difference between the ground vibrational level of the electronic ground state and the separated atoms.
- **Principle of Determination:** Extrapolation of the vibrational energy levels to their convergence limit provides the dissociation energy.

Decay of Excited States

Excited electronic states can return to lower energy states via various pathways:

- **Radiative Paths:** Emission of a photon. Examples include fluorescence and phosphorescence.
- **Non-Radiative Paths:** Energy is dissipated as heat or used to induce other molecular processes. Examples include internal conversion and intersystem crossing.

Pre-dissociation

A process where a molecule in an excited electronic state crosses over to a repulsive or dissociative potential energy curve of a higher energy state. This leads to the dissociation of the molecule without the emission of radiation. The spectral lines associated with pre-dissociation often appear broadened or even absent.

Fluorescence and Phosphorescence, Jablonskii Diagram

These are radiative decay processes from excited states:

- **Fluorescence:** Emission of light from a singlet excited state (S_1) to the ground singlet state (S_0). It is typically fast (nanoseconds to microseconds).
- **Phosphorescence:** Emission of light from a triplet excited state (T_1) to the ground singlet state (S_0). This is a spin-forbidden process, making it much slower (milliseconds to hours).

Jablonskii Diagram: A schematic representation illustrating the relative energy levels of singlet (S_0, S_1, S_2, ...) and triplet (T_1, T_2, ...) states, along with various radiative and non-radiative processes connecting them. It helps visualize fluorescence, phosphorescence, internal conversion, and intersystem crossing.

Numerical Problems on Electronic Spectroscopy

(Placeholder for numerical problems related to potential energy curves, Franck-Condon factors, bond dissociation energy calculations, and analysis of spectral data.)

II. RAMAN SPECTROSCOPY

Classical Treatment

In the classical view, Raman scattering occurs when incident light interacts with a molecule, inducing a temporary dipole moment. This induced dipole moment oscillates at the frequency of the incident light and also at vibrational and rotational frequencies of the molecule. The oscillating dipole then re-radiates energy.

- **Elastic Scattering (Rayleigh):** The induced dipole oscillates at the same frequency as the incident light, resulting in scattered light of the same frequency.
- **Inelastic Scattering (Raman):** The induced dipole oscillates at frequencies different from the incident light, corresponding to changes in the molecule's vibrational or rotational energy.

Rotational Raman Effect

This effect arises from changes in the rotational energy levels of molecules during scattering. The selection rules for rotational Raman spectra are typically $\Delta J = 0, \pm 2$, where J is the rotational quantum number.

- Stokes lines correspond to a decrease in rotational energy ($\Delta J = -2$), with scattered light having lower frequency.
- Anti-Stokes lines correspond to an increase in rotational energy ($\Delta J = +2$), with scattered light having higher frequency.

Vibrational Raman Spectra

This arises from changes in the vibrational energy levels during scattering. A vibrational mode will be Raman active if it causes a change in the molecule's polarizability during the vibration.

- **Stokes Lines:** Occur when the molecule transitions from a lower vibrational state (usually v=0) to a higher vibrational state (v=1, 2, ...). The scattered photon loses energy, resulting in a lower frequency (longer wavelength) line.
- **Anti-Stokes Lines:** Occur when the molecule transitions from a higher vibrational state (e.g., v=1) to a lower vibrational state (e.g., v=0). The scattered photon gains energy, resulting in a higher frequency (shorter wavelength) line.

Stokes and Anti-Stokes Lines: Intensity Difference

The intensity of Stokes and anti-Stokes lines depends on the population of the initial vibrational states, which is governed by the Boltzmann distribution.

- At typical temperatures, the population of the ground vibrational state (v=0) is much higher than that of the first excited state (v=1).
- Therefore, Stokes lines (originating from v=0) are generally much more intense than anti-Stokes lines (originating from v=1). The intensity difference increases with decreasing temperature.

Rule of Mutual Exclusion

This rule applies to molecules that possess a center of symmetry. It states that vibrational modes that are Raman active are infrared inactive, and vice versa.

- Symmetric vibrations (e.g., stretching of bonds in molecules like CO_2 or C_2H_4) are typically Raman active and IR inactive.
- Asymmetric vibrations are often IR active and Raman inactive.
- For molecules without a center of symmetry, some vibrations may be both Raman and IR active.

Numerical Problems on Raman Spectroscopy

(Placeholder for numerical problems related to rotational Raman shifts, vibrational Raman shifts, intensity calculations, and application of the rule of mutual exclusion.)