DETAILED STUDY MATERIAL: ROTATION AND VIBRATIONAL SPECTROSCOPY WITH NUMERICAL PROBLEM EXAMPLES

1. ROTATION SPECTROSCOPY

This section covers the principles, selection rules, intensity factors, and applications of rotational spectroscopy for determining molecular structures.

1.1 Introduction to Rotation Spectroscopy

Rotation spectroscopy, also known as microwave spectroscopy, probes the rotational energy levels of molecules. These transitions occur in the microwave region of the electromagnetic spectrum. It is primarily used for studying the structure of small molecules in the gas phase.

1.2 Selection Rules for Rotational Spectroscopy

For a molecule to exhibit pure rotational absorption or emission spectra, it must possess a permanent dipole moment.

The selection rules for diatomic molecules are:

- **$\Delta J = \pm 1$**: The rotational quantum number J can change by plus or minus one unit.
- **$\Delta J = +1$** corresponds to absorption, and **$\Delta J = -1$** corresponds to emission.

For linear, symmetric top, and spherical top molecules, the selection rules are:

- **Diatomic and Linear Molecules:** $\Delta J = \pm 1$
- **Symmetric Top Molecules:** $\Delta J = 0, \pm 1$; $\Delta K = 0$
- **Spherical Top Molecules:** Generally do not show pure rotational spectra as they lack a permanent dipole moment unless degenerate levels are involved and perturbed.

1.3 Intensities of Spectral Lines

The intensity of a spectral line is proportional to:

- **Population of the initial energy level:** According to the Boltzmann distribution, higher populated levels lead to stronger transitions.
- **Transition probability:** Governed by the selection rules and the dipole moment of the molecule.

Boltzmann Distribution: The population of a rotational level *J* is given by:

$$N_J / N_{total} = (2J + 1) * \exp(-E_J / kT) / Q_{rot}$$

where $E_J = BJ(J+1)$ for diatomic molecules (in appropriate units), k is the Boltzmann constant, T is the absolute temperature, and Q_{rot} is the rotational partition function.

1.4 Determination of Bond Lengths

1.4.1 Diatomic Molecules

The energy levels of a rigid diatomic rotor are given by:

$$E_J = B J (J+1)$$

where **B** is the rotational constant, related to the moment of inertia (I) by $B = h / (8\pi^2 cI)$. The moment of inertia for a diatomic molecule is $I = \mu r^2$, where **μ** is the reduced mass and **r** is the bond length.

Numerical Problem Example:

A diatomic molecule exhibits a rotational spectrum with lines spaced 2 cm^{-1}. Calculate the bond length of the molecule. (Given: $h = 6.626 \times 10^{-34}$ J·s, $c = 3 \times 10^{10}$ cm/s, Avogadro's number $N_A = 6.022 \times 10^{23}$ mol^{-1}). Assume the molecule is HCl.

Steps to solve:

1. Determine the rotational constant B from the spacing of spectral lines.
2. Calculate the moment of inertia I using B.
3. Calculate the reduced mass μ for the given molecule.

4. Calculate the bond length r using $I = \mu r^2$.

1.4.2 Linear Triatomic Molecules

For linear triatomic molecules, the concept of a single bond length is extended to internuclear distances. The molecule can rotate about an axis perpendicular to the molecular axis. The moment of inertia calculation becomes more complex, involving the masses and positions of all atoms.

Numerical Problem Example:

Consider the molecule OCS. If its rotational constant is $B = 0.155\ \text{cm}^{-1}$, determine its moment of inertia and discuss how isotopic substitution (e.g., ^{18}O substitution) could help determine individual bond lengths (CO and CS).

Steps to solve:

1. Calculate the moment of inertia from B.
2. For linear molecules, $I = \Sigma m_i r_i^2$, where m_i is the mass of atom i and r_i is its distance from the center of mass.
3. Set up equations for different isotopic substitutions and solve for the internuclear distances.

1.5 Isotopic Substitution

Observing the rotational spectra of molecules with different isotopes can be very powerful for structure determination. Since the electronic structure remains largely unchanged, isotopic substitution primarily affects the moment of inertia and thus the rotational constant B. By comparing the B values of isotopically substituted molecules, one can often determine internuclear distances and even distinguish between different isomers.

2. VIBRATIONAL SPECTROSCOPY

This section delves into the classical and quantum mechanical descriptions of molecular vibrations, including force constants, anharmonicity, potential energy surfaces, and the nature of vibrational spectra.

2.1 Classical Equation of Vibration (Harmonic Oscillator Model)

A diatomic molecule can be approximated as two masses (m_1 and m_2) connected by a spring. The motion is described by the harmonic oscillator model, where the restoring force is proportional to the displacement from equilibrium:

$$F = -kx$$

where **k** is the force constant and **x** is the displacement. The angular frequency of vibration (ω) is given by:

$$\omega = \sqrt{(k/\mu)}$$

where **μ** is the reduced mass ($\mu = m_1 m_2 / (m_1 + m_2)$). The frequency in cm^{-1} (wavenumber, $\tilde{\nu}$) is related by $\omega = 2\pi c\tilde{\nu}$.

2.2 Computation of Force Constant

From the vibrational frequency ($\tilde{\nu}$) of a diatomic molecule, the force constant (k) can be calculated:

$$k = 4\pi^2 c^2 \mu \tilde{\nu}^2$$

Numerical Problem Example:

The vibrational frequency of $^1H^{35}Cl$ is 2990 cm^{-1}. Calculate the force constant of the bond. (Given: μ for $^1H^{35}Cl \approx 0.98 \times 10^{-27}$ kg, $c = 2.998 \times 10^{10}$ cm/s).

Steps to solve:

1. Ensure all units are consistent (e.g., kg for mass, cm/s for c).
2. Plug the values into the formula for k.

2.3 Amplitude of Diatomic Molecular Vibrations

The amplitude of vibration refers to the maximum displacement of the atoms from their equilibrium positions. For a harmonic oscillator, the amplitude is quantized and depends on the vibrational energy level.

2.4 Anharmonicity and Morse Potential

Real molecular potentials are anharmonic, meaning the restoring force is not strictly proportional to displacement, especially at larger displacements. The Morse potential is a more realistic model:

$$V(r) = D_e [1 - \exp(-a(r - r_e))]^2$$

where D_e is the dissociation energy (well depth), r_e is the equilibrium bond length, and 'a' is a constant related to the force constant.

2.5 Dissociation Energies

The Morse potential provides a good approximation for the dissociation energy (D_e), representing the energy required to break the bond from its lowest vibrational state.

The energy levels for a Morse oscillator are given by:

$$G(v) = (v + 1/2)\hbar\omega_e - (v + 1/2)^2 \hbar\omega_e x_e$$

where v is the vibrational quantum number, ω_e is the harmonic frequency, and x_e is the anharmonicity constant.

Numerical Problem Example:

A diatomic molecule has G(0) = 0.52 eV and G(1) = 1.53 eV. Calculate its harmonic frequency (ω_e) and anharmonicity constant (x_e). Also, estimate its dissociation energy if the force constant is 500 N/m.

Steps to solve:

1. Use the G(v) equations for v=0 and v=1 to form two equations with two unknowns ($\hbar\omega_e$ and $\hbar\omega_e x_e$).
2. Solve these equations.
3. Relate D_e to the harmonic and anharmonic terms.

2.6 Fundamental Frequencies, Overtones, and Hot Bands

- **Fundamental Frequencies:** Transitions from v=0 to v=1 ($\Delta v = +1$). These are typically the strongest vibrational bands.

- **Overtones:** Transitions from v=0 to higher levels (Δv = +2, +3, etc.). These are weaker due to anharmonicity.
- **Hot Bands:** Transitions originating from excited vibrational states (e.g., v=1 to v=2). These become more significant at higher temperatures as the population of excited states increases.

2.7 Degrees of Freedom for Polyatomic Molecules

For a non-linear molecule with N atoms, there are 3N degrees of freedom. These are divided into:

- 3 translational degrees of freedom (motion of the center of mass).
- 3 rotational degrees of freedom (rotation about x, y, z axes).
- 3N - 6 vibrational degrees of freedom (normal modes of vibration).

For a linear molecule with N atoms, there are 3N-5 vibrational degrees of freedom.

2.8 Modes of Vibration

These are the independent ways a molecule can vibrate. Each normal mode has a specific frequency and can be observed in the IR and Raman spectra.

2.9 Diatomic Vibrating Rotator

This model considers a molecule that can simultaneously vibrate and rotate. The energy levels are approximated by combining vibrational and rotational energy, leading to vibrational-rotational spectra.

$E(v, J) \approx (v + 1/2)\hbar\omega_e - (v + 1/2)^2 \hbar\omega_e x_e + BJ(J+1)$ (for a harmonic oscillator, B is often J-dependent in more advanced models, but this gives the basic idea).

2.10 P, Q, R Branches

In vibrational-rotational spectra, transitions involve changes in both vibrational (Δv) and rotational (ΔJ) quantum numbers.

- **R-branch:** ΔJ = +1 (rotational quantum number increases).

- **P-branch:** ΔJ = -1 (rotational quantum number decreases).
- **Q-branch:** ΔJ = 0 (rotational quantum number remains the same). This branch is only allowed if the molecule's symmetry permits it or if there is a change in the component of the dipole moment along the bond axis during vibration (e.g., in symmetric top molecules). For linear molecules, the Q branch is typically forbidden for vibrational transitions that do not involve a change in angular momentum along the molecular axis.

The spacing between lines in the P and R branches is approximately 2B.