

STRUCTURAL INVESTIGATION OF MOLECULES

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Abstract:

Raman spectroscopy is one of the important tools to investigate the molecular structures. Raman excitation profile studies help us enormously in understanding the same. Different aromatic molecules have been chosen. In this section theoretical approach that is time dependent perturbation theory has been discussed accordingly.

Introduction:

Electromagnetic radiation interacts with matter in many ways. One of them is Raman Scattering. Different types of Raman Scattering like Normal Raman scattering, Resonance Raman Scattering etc. can throw light on different aspect. Normal Raman Scattering is the phenomenon relating the scattering of light by molecular energy state. Normal Raman Scattering can be properly understood by perturbation theory. According to perturbation theory during perturbation the molecular energy level becomes the summation of different energy eigen states. Critical studies of Normal Raman Spectra can provide much purposeful information. With the help of time dependent perturbation (Kramers-Heisenberg-Dirac theory) theory the intensity of spectral line can be determined.

Time dependent perturbation theory:

Scattering intensity I_s (in number of photons per molecule per second) of a Raman line of angular frequency ω_s , for a molecular transition from the initial state $|G\rangle$ to a final state $|F\rangle$ is given by,

$$I_s = K' \omega_s^3 I_0 \sum_{\rho, \sigma} \left| \langle \alpha_{\rho\sigma} \rangle_{GF} \right|^2$$

where K' is a constant, I_0 is the intensity of the incident laser radiation of angular frequency ω_0 , $\langle \alpha_{\rho\sigma} \rangle_{GF}$ is the polarizability (scattering) tensor of the transition from

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vibronic state G to vibronic state F with the incident and scattered polarizations indicated by ρ and σ ($\rho, \sigma = x, y, z$) respectively. Here averaging over all orientations has been considered. For molecules with no absorption band in the visible or near ultraviolet region, the scattering tensor $\langle \alpha_{\rho\sigma} \rangle_{GF}$ is nearly a constant and so Raman intensities in these molecules depend on the fourth power of the scattered frequencies (ν_s^4), just like Rayleigh Scattering. But for molecules having absorption bands in the visible or near ultraviolet region, $\langle \alpha_{\rho\sigma} \rangle_{GF}$ no longer remains constant but depends on various properties of the excited state potentials. Since the scattering intensity is proportional to the square of the scattering tensor, so the study of intensity pattern of different Raman bands and their variation with the change of excitation frequency (called Raman excitation profiles i.e. REPs) may unravel many intricate characteristics of the molecule in various excited electronic states.

With the help of time-dependent perturbation theory [Kramers-Heisenberg-Dirac (KHD) theory], it can be shown that (ρ, σ)-th component of the polarizability matrix between the initial and final states is,

$$\langle \alpha_{\rho\sigma} \rangle_{GF} = \frac{1}{\eta} \sum_I \frac{\langle F | P_\rho | I \rangle \langle I | P_\sigma | G \rangle}{\omega_{IG} - \omega_0 - i\Gamma_I} + \frac{\langle F | P_\sigma | I \rangle \langle I | P_\rho | G \rangle}{\omega_{IF} + \omega_0 - i\Gamma_I}$$

Here $|I\rangle$ is an intermediate state of the molecule. Γ_I is the damping term reflecting the homogeneous width of the state $|I\rangle$. For simplicity we have not included the effect of damping of the initial and final states $|G\rangle$ and $|F\rangle$. $P_{\rho\sigma}$ is the ρ, σ -th component of the electric dipole moment of the molecule. Since we are interested about vibrational Raman scattering, all the states $|G\rangle$, $|F\rangle$, $|I\rangle$ are considered to be vibronic states.

According to Born-Oppenheimer approximation,

$$|I\rangle = \Psi_{Ii}(q, Q) = \Theta_I(q, Q) U_i(Q)$$

$$|G\rangle = \Psi_{Gm}(q, Q) = \Theta_G(q, Q) U_m(Q)$$

$$|F\rangle = \Psi_{Fn}(q, Q) = \Theta_G(q, Q) U_n(Q)$$

where q represents the set of electronic coordinates and Q the set of nuclear (normal) coordinates, Θ 's and U 's are electronic and vibrational wavefunctions. All

capital and small letters in the subscripts correspond to electronic and vibrational states respectively. Moreover for vibrational Raman scattering, the initial and final vibrational states, $|m\rangle$ and $|n\rangle$, correspond to the same electronic state ($|G\rangle$).

$$\begin{aligned} \text{Therefore } \langle F|P_\rho|I\rangle &= \iint [\Theta_G(q, Q)U_n(Q)]^* P_\rho [\Theta_I(q, Q)U_i(Q)] dq dQ \\ &= \int [U_n(Q)]^* \langle P_\rho(Q) \rangle_{GI} U_i(Q) dQ \end{aligned}$$

where $\langle P_\rho(Q) \rangle_{GI} = \int [\Theta_G(q, Q)]^* P_\rho \Theta_I(q, Q) dq$ is electric transition dipole moment for the transition $G \leftrightarrow I$, at nuclear configuration Q .

This electric transition dipole moment $\langle P_\rho(Q) \rangle_{GI}$ will vary with the nuclear displacement during execution of any normal mode of vibration.

Nuclear coordinate dependence of the electronic wave functions may be expanded following Herzberg-Teller (HT) approximation. The electronic Hamiltonian (H) in the field of a given nuclear configuration (Q_k) is given by,

$$\begin{aligned} H &= -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,k} \frac{Z_k e^2}{r_{ik}} + \sum_i \sum_{<j} \frac{e^2}{r_{ij}} \\ &= H_0 + \sum_k \left(\frac{\partial H}{\partial Q_k} \right)_0 (Q_k - Q_k(0)) = H_0 + \sum_k \left(\frac{\partial H}{\partial Q_k} \right)_0 Q_k \end{aligned}$$

Here H_0 is the unperturbed part of the electronic Hamiltonian arising from the interaction of electrons with electrons and nuclei in a fixed (equilibrium) nuclear configuration ($Q_k(0)$), m_e is the mass of the electron, Z_k is the atomic number of the k -th nucleus, r_{ij} is the distance between the i^{th} and j^{th} electrons. Also r_{ik} is the distance between the i^{th} electron and k^{th} nucleus. Equilibrium values of all the normal coordinates are assumed to be zero i.e. $Q_k(0) = 0$ for all ks .

So the perturbed electronic wavefunction becomes,

$$|I(q, Q)\rangle = |I(q, Q_0)\rangle + \sum_k \sum_{S \neq I} \frac{\langle S | \left(\frac{\partial H}{\partial Q_k} \right) | I \rangle_0}{E_I^0 - E_S^0} Q_k |S(q, Q_0)\rangle$$

Here suffix "0" corresponds to equilibrium nuclear configuration of the molecule and we have considered only first order perturbation. The second term on the right hand

side of equation indicates mixing of electronic states $|I\rangle$ and $|S\rangle$ through the differential operator $\left(\frac{\partial H}{\partial Q_k}\right)$.

Substituting this in the expression for $\langle F|P_\rho|I\rangle$, the transition dipole moment

$$\langle F|P_\rho|I\rangle \quad \text{becomes, } \langle F|P_\rho|I\rangle = \langle p_\rho(Q_k) \rangle_{GI}^0 + \sum_k \sum_{S \neq I} \frac{\langle S | \left(\frac{\partial H}{\partial Q_k} \right) | I \rangle_0}{E_I^0 - E_S^0} \langle P_\rho(Q_k) \rangle_{GS}^0 \langle n|Q_k|i \rangle$$

We have neglected the mixing of the ground state with other electronic states because of the large value of the energy differences $(E_G^0 - E_S^0)$ appearing in the denominator of the mixing part of the perturbed wave function. We can have similar expressions for $\langle I|P_\sigma|G\rangle$, $\langle F|P_\sigma|I\rangle$, and $\langle I|P_\rho|G\rangle$, where $\rho, \sigma = x, y, z$. Thus we have,

$$\langle \alpha_{\rho\sigma} \rangle_{GF} = A + B$$

The first term appears due to the contribution from Frank-Condon overlap integral and the second term appears due to the mixing of two electronic states and is known as Herzberg-Teller term.

The A term [changing all the angular frequencies ω_s into the corresponding wavenumbers $\tilde{\nu}_s$ by the relation $\omega = 2\pi c \tilde{\nu}$] is given by,

$$A = (ch)^{-1} \sum_I \langle P_\rho \rangle_{GI}^0 \langle P_\sigma \rangle_{IG}^0 \sum_i \left[\frac{1}{\tilde{\nu}_{IiGm} - \tilde{\nu}_0 - i\tilde{\Gamma}_{Ii}} + \frac{1}{\tilde{\nu}_{IiGn} + \tilde{\nu}_0 - i\tilde{\Gamma}_{Ii}} \right] \times \langle n|i \rangle \langle i|m \rangle$$

For excitation of the fundamental vibration in the Raman spectra, the A-term becomes,

$$A = (ch)^{-1} \sum_I \langle P_\rho \rangle_{GI}^0 \langle P_\sigma \rangle_{IG}^0 \sum_i \left[\frac{1}{\tilde{\nu}_{IiG0} - \tilde{\nu}_0 - i\tilde{\Gamma}_{Ii}} + \frac{1}{\tilde{\nu}_{IiG1} + \tilde{\nu}_0 - i\tilde{\Gamma}_{Ii}} \right] \times \langle 1|i \rangle \langle i|0 \rangle$$

Here $ch\tilde{\nu}_{IiG0} = E(Ii) - E(G0)$ and $ch\tilde{\nu}_{IiG1} = E(Ii) - E(G1)$. $\langle 1|i \rangle$ and $\langle i|0 \rangle$ are vibrational overlap integrals. Since we are considering Raman intensities of only fundamental vibration, '1' and '0' in the vibrational overlap integrals refer to vibrational quantum numbers of the respective vibrations in the ground electronic

state. $\tilde{\Gamma}_{Ii}$ is the half width of the vibronic state $|Ii\rangle$ in wavenumber unit. For excitation of the k-th fundamental mode, the multimode expression for the overlap integral part in the above expression for A becomes (under the assumption of no Duschinsky's mixing),

$$\langle 1|i\rangle\langle i|0\rangle = \langle 1_k|i_k\rangle\langle i_k|0_k\rangle \times \prod_{j \neq k} \langle 0_j|i_j\rangle\langle i_j|0_j\rangle$$

Overlap factors may be determined on the basis of a simple harmonic oscillator type vibrational wavefunctions. The overlap integral, obtained from the recurrence relation of Manneback, is found to be a function of the displacement of the excited state potential minimum of the concerned electronic state with respect to that of the ground electronic state along the concerned normal coordinate (say k-th) i.e. $\Delta_k^I = (Q_{kI} - Q_{kG})_0$ and of the wavenumbers $(\tilde{\nu}_k)_G$ and $(\tilde{\nu}_k)_I$ of the corresponding normal mode (k-th) in the ground and excited electronic states respectively.

In the case of a small displacement of the excited state potential minimum with respect to that of the ground state,

$$\begin{aligned} \langle 1_k|i_k\rangle\langle i_k|0_k\rangle &= \Delta_k^I \text{ for } i_k = 0 \\ &= -\Delta_k^I \text{ for } i_k = 1 \end{aligned}$$

and also

$$\begin{aligned} \langle 0|i_j\rangle\langle i_j|0\rangle &= 1 \text{ for } i_j = 0 \\ &= 0 \text{ for } i_j \geq 1 \end{aligned}$$

Thus equation of A reduces to,

$$A = (ch)^{-1}$$

$$\sum_I \langle P_\rho \rangle_{GI}^0 \langle P_\sigma \rangle_{IG}^0 \tilde{\nu}_k \Delta_k^I \times \left[\frac{1}{(\tilde{\nu}_{IG} - \tilde{\nu}_0 - i\tilde{\Gamma}_I)(\tilde{\nu}_{IG} + \tilde{\nu}_k - \tilde{\nu}_0 - i\tilde{\Gamma}_I)} + \frac{1}{(\tilde{\nu}_{IG} + \tilde{\nu}_0 - i\tilde{\Gamma}_I)(\tilde{\nu}_{IG} - \tilde{\nu}_k + \tilde{\nu}_0 - i\tilde{\Gamma}_I)} \right]$$

It is assumed that $(\tilde{\nu}_k)_G = (\tilde{\nu}_k)_I = (\tilde{\nu}_k)$ and $\tilde{\Gamma}_{Ii} = \tilde{\Gamma}_I$ for all i s. For excitation far from resonance (i.e. for normal Raman scattering), $(\tilde{\nu}_k)$ and Γ_I can be neglected in comparison with $\tilde{\nu}_{IG} \pm \tilde{\nu}_0$ appearing on the denominators of equation and thus the

$$\text{above equation reduces to, } A = \frac{2}{ch} \sum_I \langle P_\rho \rangle_{GI}^0 \langle P_\sigma \rangle_{IG}^0 \tilde{\nu}_k \Delta_k^I \times \frac{\tilde{\nu}_{IG}^2 + \tilde{\nu}_0^2}{(\tilde{\nu}_{IG}^2 - \tilde{\nu}_0^2)^2}$$

For a similar kind of excitation it can be shown that the other term B becomes,

$$B \quad \quad \quad = \quad \quad \quad \frac{2}{(ch)^2}$$

$$\sum_I \sum_{\langle S \rangle} \left[\langle P_\rho \rangle_{GI}^0 h_{IS}^k \langle P_\sigma \rangle_{SG}^0 + \langle P_\rho \rangle_{GS}^0 h_{SI}^k \langle P_\sigma \rangle_{IG}^0 \right] \times \frac{\tilde{\nu}_{IG} \tilde{\nu}_{SG} + \tilde{\nu}_0^2}{(\tilde{\nu}_{IG}^2 - \tilde{\nu}_0^2)(\tilde{\nu}_{SG}^2 - \tilde{\nu}_0^2)} \langle 1_k | Q_k | 0_k \rangle$$

$$\text{where } h_{IS}^k = \left\langle I \left| \left(\frac{\partial H}{\partial Q_k} \right) \right| S \right\rangle_0.$$

A good knowledge about the normal modes (Q_k s) and critical study on the variation of intensities of different Raman bands with the change of excitation frequency (i.e. Raman excitation profile study) may provide information about molecular structures in the excited electronic states in terms of Δ_k^I , which is a measure of molecular distortion in the I-th electronic state with respect to that of the ground electronic state along k-th normal mode of vibration (Q_k). This type of investigation may also throw light on the nature of vibronic interaction between various pairs of excited electronic states. For totally symmetric vibrations, only diagonal components of the polarizability tensor ($\alpha_{\rho\rho}$) are expected to take part in the scattering phenomena and in that case Raman intensity for the k-th normal mode, when measured in terms of a quantity proportional to the number of the scattered photons, becomes,

$$I_S = K(\tilde{\nu}_0 - \tilde{\nu}_k)^3 I_0 \sum_\rho \left| \langle \alpha_{\rho\rho} \rangle \right|^2$$

$$= K(\tilde{\nu}_0 - \tilde{\nu}_k)^3 I_0 \left[\sum_I F_A \tilde{\nu}_k \Delta_k^I \frac{\tilde{\nu}_{IG}^2 + \tilde{\nu}_0^2}{(\tilde{\nu}_{IG}^2 - \tilde{\nu}_0^2)} + \sum_I \sum_{\langle S \rangle} F_B \frac{\tilde{\nu}_{IG} \tilde{\nu}_{SG} + \tilde{\nu}_0^2}{(\tilde{\nu}_{IG}^2 - \tilde{\nu}_0^2)(\tilde{\nu}_{SG}^2 - \tilde{\nu}_0^2)} \right]^2$$

$$\text{where } F_A = \frac{2}{ch} \langle P_\rho \rangle_{GI}^0 \langle P_\sigma \rangle_{IG}^0 \text{ and}$$

$$F_B = \frac{2}{(ch)^2} \left[\langle P_\rho \rangle_{GI}^0 h_{IS}^k \langle P_\sigma \rangle_{SG}^0 + \langle P_\rho \rangle_{GS}^0 h_{SI}^k \langle P_\sigma \rangle_{IG}^0 \right] \langle 1_k | Q_k | 0_k \rangle.$$

Conclusion:

Thus polarizability tensor plays important role in studies of Raman Spectra. We see that polarizability tensor has dependence on several parametric values of one or more electronic states. The analyses of variation of Raman intensities with the change of excitation wavelengths may yield information about the concerned electronic states. This is called Raman excitation profile. In case of Normal Raman Scattering we get the structural insights of molecule in the ground state. But in Raman excitation profile we get the idea of molecule in their excited states.

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