

The Raman Effect

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I. INTRODUCTION

Raman scattering is widely used to study the vibrational and rotational properties of molecules. Normally infrared spectroscopy is needed to probe these levels but because of the Raman effect it is possible to excite these levels using visible light. In some cases Raman scattering is the only way to study these transitions. An example of this is the molecule H_2 . Since this molecule has no electric dipole (even in excited vibrational states) it will not radiate and we will see no emission line for this transition.

Raman scattering is very closely related to Rayleigh scattering. In both cases light with more than enough energy to excite any vibrational or rotational states, but not enough energy to bring it out of the ground electronic state, is shined on the molecule. This light then excites the molecule to a virtual state that then decays back down to lower energy states. In Rayleigh scattering the molecule decays back to the initial state, figure (1), and in Raman scattering it decays to different state. When the final energy state is higher than the original state it is called a Stokes transition, figure (2), and when the final state is lower it is called an anti-Stokes transition. The light that is emitted in the de-excitation can then be studied.

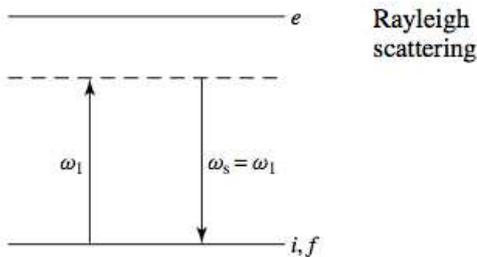


FIG. 1: Rayleigh Scattering. Image taken from *The Raman Effect* [3]

In this paper we will first work through the classical approach to the Raman effect. Next a full quantum mechanical treatment of the problem is addressed. To study these results some simplifying assumptions

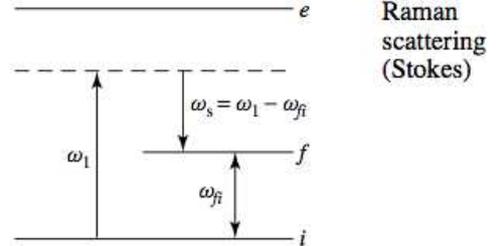


FIG. 2: Stokes Raman Scattering. Image taken from *The Raman Effect* [3]

will be made. And finally we will look at vibrational and rotational Raman transitions.

II. CLASSICAL APPROACH TO THE RAMAN EFFECT

In this section we will explore the classical nature of Raman effect. When a photon interacts with a molecule it will cause the electrons and protons to move and this will induce an oscillating dipole. This dipole will then radiate photons of different frequencies.

To find these frequencies we start with a photon with the following electric field:

$$\vec{E} = \vec{E}_0 \cos(\omega_0 t) \quad (1)$$

The induced dipole will then look like:

$$P_\rho = \alpha_{\rho\sigma} E_\sigma = \alpha_{\rho\sigma} E_{\sigma 0} \cos(\omega_0 t) \quad (2)$$

Where $\alpha_{\rho\sigma}$ is the polarizability tensor of the molecule. This is a measure of how easy it is to polarize the molecule along each direction. Throughout this paper I will be using Einstein notation (an implied sum over repeated indices). This α does not have a constant value, it depends on the shape of the molecule.

For small displacements the polarizability tensor can be expanded as a Taylor series in the normal coordinates of the molecule:

$$\alpha_{\rho\sigma}(Q) = (\alpha_{\rho\sigma})_0 + \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 Q_k + \dots \quad (3)$$

Where $(\alpha_{\rho\sigma})_0$ is the polarizability tensor at the equilibrium configuration and Q_k is the k^{th} normal mode coordinate of the molecule associated with the vibrational frequency ω_k . Since the normal modes are harmonic Q can be written as:

$$Q_k = Q_{k0} \cos(\omega_k t) \quad (4)$$

Plugging this into eqn. (3) and placing that into eqn. (2) will give the linear induced dipole vector $\vec{P}^{(0)}$:

$$\begin{aligned} P_\rho^{(0)} &= (\alpha_{\rho\sigma})_0 E_{\sigma 0} \cos(\omega_0 t) + \\ &+ \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 Q_{k0} E_{\sigma 0} \cos(\omega_k t) \cos(\omega_0 t) \\ &= (\alpha_{\rho\sigma})_0 E_{\sigma 0} \cos(\omega_0 t) \\ &+ \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 \frac{Q_{k0} E_{\sigma 0}}{2} [\cos(t(\omega_0 - \omega_k)) \\ &+ \cos(t(\omega_0 + \omega_k))] \end{aligned} \quad (5)$$

This clearly show that the dipole contains three frequencies ω_0 , $\omega_0 - \omega_k$, and $\omega_0 + \omega_k$. These give rise to Rayleigh, Stokes, and anti-Stokes scattering respectively.

III. FULL QUANTUM MECHANICAL TREATMENT

In this section we will treat the incoming photon as a source of a time-dependent perturbation on the energy levels of the molecule.

We start with the unperturbed time-dependent wave function for the molecule:

$$\Psi_r^{(0)} = \psi_r \exp -it(\omega_j - i\Gamma_r) \quad (6)$$

Where Γ_r is related to the half-width half-height or the transition line and the lifetime of the state $\tau \propto \frac{1}{2\Gamma_r}$. The perturbed wave function can be expressed in this form:

$$\Psi_r' = \Psi_r^{(0)} + \Psi_r^{(1)} + \dots \quad (7)$$

From this we can define the electric dipole transition moment for the transition $f \leftarrow i$ when the system is perturbed:

$$(P)_{fi} = \langle \Psi_f' | \hat{P} | \Psi_i' \rangle \quad (8)$$

Placing eqn. (7) into eqn. (8) and collecting terms of similar order:

$$(P)_{fi} = (P^{(0)})_{fi} + (P^{(1)})_{fi} + \dots \quad (9)$$

where

$$(P^{(0)})_{fi} = \langle \Psi_f^{(0)} | \hat{P} | \Psi_i^{(0)} \rangle \quad (10)$$

$$(P^{(1)})_{fi} = \langle \Psi_f^{(1)} | \hat{P} | \Psi_i^{(0)} \rangle + \langle \Psi_f^{(0)} | \hat{P} | \Psi_i^{(1)} \rangle \quad (11)$$

The leading order term of the expansion relates to a direct transition from the unperturbed initial and final states. The first order correction relates to the induced electric dipole. All higher order terms relate to higher order terms in the multipole expansion. It is the first term that gives rise to both Rayleigh and Raman scattering and that is the one we will look at more closely.

Using first order time-dependent perturbation theory:

$$\Psi_i^{(1)} = \sum_r a_{ir} \Psi_r^{(0)} \text{ and } \Psi_f^{(1)} = \sum_r a_{fr} \Psi_r^{(0)} \quad (12)$$

Placing this into eqn. (11):

$$(\tilde{P}^{(1)})_{fi} = \sum_r a_{fr}^* \langle \Psi_r^{(0)} | \hat{P} | \Psi_i^{(0)} \rangle + \sum_r a_{ir} \langle \Psi_f^{(0)} | \hat{P} | \Psi_r^{(0)} \rangle \quad (13)$$

Where the tilde above the P is a reminder that this term is in general complex.

The coefficients are then given by the perturbation Hamiltonian generated by the incoming photon:

$$a_{ir} = -\frac{i}{\hbar} \int_0^t \langle \Psi_r^{(0)} | H_p | \Psi_i^{(0)} \rangle dt' \quad (14)$$

$$a_{fr}^* = \frac{i}{\hbar} \int_0^t \langle \Psi_f^{(0)} | H_p | \Psi_r^{(0)} \rangle dt' \quad (15)$$

$$H_p = -\hat{P}_\sigma E_\sigma \quad (16)$$

$$E_\sigma = \tilde{E}_{\sigma 0} \exp(-it\omega_0) + \tilde{E}_{\sigma 0}^* \exp(it\omega_0) \quad (17)$$

Now we have to place eqn. (6) in these equations. Since the lifetime of the initial and final states are taken to be infinite $\Gamma_i = \Gamma_f = 0$.

$$\begin{aligned}
(\tilde{P}^{(1)})_{fi} = & \frac{1}{\hbar} \sum_{r \neq f,i} \left[\frac{\langle \psi_f^{(0)} | \hat{P}_\sigma | \psi_r^{(0)} \rangle \langle \psi_r^{(0)} | \hat{P}_\rho | \psi_i^{(0)} \rangle}{\omega_{rf} - \omega_0 - i\Gamma_r} + \frac{\langle \psi_f^{(0)} | \hat{P}_\rho | \psi_r^{(0)} \rangle \langle \psi_r^{(0)} | \hat{P}_\sigma | \psi_i^{(0)} \rangle}{\omega_{ri} + \omega_0 + i\Gamma_r} \right] \tilde{E}_{\sigma 0}^* \exp [it(\omega_0 + \omega_{fi})] \\
& + \frac{1}{\hbar} \sum_{r \neq f,i} \left[\frac{\langle \psi_f^{(0)} | \hat{P}_\sigma | \psi_r^{(0)} \rangle \langle \psi_r^{(0)} | \hat{P}_\rho | \psi_i^{(0)} \rangle}{\omega_{rf} + \omega_0 + i\Gamma_r} + \frac{\langle \psi_f^{(0)} | \hat{P}_\rho | \psi_r^{(0)} \rangle \langle \psi_r^{(0)} | \hat{P}_\sigma | \psi_i^{(0)} \rangle}{\omega_{ri} - \omega_0 - i\Gamma_r} \right] \tilde{E}_{\sigma 0} \exp [-it(\omega_0 - \omega_{fi})]
\end{aligned} \quad (18)$$

Where

$$\omega_{rf} = \omega_r - \omega_f \quad (19)$$

The radiation dipole that is associated with this complex transition moment is:

$$(P^{(1)})_{fi} = (\tilde{P}^{(1)})_{fi} + (\tilde{P}^{(1)})_{fi}^* \quad (20)$$

There are two frequency dependencies in the transition moment, $(\omega_0 - \omega_{fi})$ and $(\omega_0 + \omega_{fi})$. The $(\omega_0 - \omega_{fi})$ term will only be associated with real radiation if $(\omega_0 - \omega_{fi}) > 0$. This is always true if initial state is lower then or equal to the final state. If the final state is lower then as long as the photon has an energy larger then the energy gap between the initial and final state this will be true. This term take care of both Rayleigh and Raman scattering.

The $(\omega_0 + \omega_{fi})$ term will only be associated with real radiation if $(\omega_0 + \omega_{fi}) > 0$. For photons in the visible part of the spectrum this means that the initial state must be an excited electronic state, and since we are only interested in scattering off of molecules starting in the ground state we not look at these terms.

From this we can now define a general transition polarizability tensor:

$$\begin{aligned}
(\alpha_{\rho\sigma})_{fi} = & \frac{1}{\hbar} \sum_{r \neq f,i} \left[\frac{\langle \psi_f^{(0)} | \hat{P}_\sigma | \psi_r^{(0)} \rangle \langle \psi_r^{(0)} | \hat{P}_\rho | \psi_i^{(0)} \rangle}{\omega_{rf} + \omega_0 + i\Gamma_r} \right. \\
& \left. + \frac{\langle \psi_f^{(0)} | \hat{P}_\rho | \psi_r^{(0)} \rangle \langle \psi_r^{(0)} | \hat{P}_\sigma | \psi_i^{(0)} \rangle}{\omega_{ri} - \omega_0 - i\Gamma_r} \right] \quad (21)
\end{aligned}$$

In general this term is complex, but by choosing ω_0 carefully it can become real. Once this is done we can treat this term as the polarizability tensor from the classical analysis.

IV. SIMPLIFICATIONS

Eqn. (21) can be written in terms of an operator:

$$(\alpha_{\rho\sigma})_{fi} = \langle \psi_f^{(0)} | \hat{\alpha}_{\rho\sigma} | \psi_i^{(0)} \rangle \quad (22)$$

$$\begin{aligned}
\hat{\alpha}_{\rho\sigma} = & \frac{1}{\hbar} \sum_{r \neq f,i} \left[\frac{\hat{P}_\sigma | \psi_r^{(0)} \rangle \langle \psi_r^{(0)} | \hat{P}_\rho}{\omega_{rf} + \omega_0 + i\Gamma_r} \right. \\
& \left. + \frac{\hat{P}_\rho | \psi_r^{(0)} \rangle \langle \psi_r^{(0)} | \hat{P}_\sigma}{\omega_{ri} - \omega_0 - i\Gamma_r} \right] \quad (23)
\end{aligned}$$

In order to make this operator easier to deal with we will make a series of approximations.

The first we make the adiabatic approximation:

$$|\psi_j\rangle = |e^j\rangle |v^j\rangle |R^j\rangle \quad (24)$$

$$\omega_j = \omega_{e^j} + \omega_{v^j} + \omega_{R^j} \quad (25)$$

That is the total wavefunction is separable into three parts: electronic, vibrational, and rotational.

For most Raman experiments the molecule starts and ends in the ground electronic state. Also the frequency of light used is chosen such that $\omega_{e^r e^g} \gg \omega_0 \gg \omega_{v^r v^i}$ and $\omega_{v^r v^f}$. That is the light has more then enough energy to excite any vibrational state but not enough to excite any electronic states. Using these assumptions it can be shown that to lowest order $\hat{\alpha}_{\rho\sigma}$ is only a function of the normal coordinates, Q , of the molecule. The last assumption that is made is that the ground state of the molecule is non-degenerate.

After all of this what we are left with is:

$$(\alpha_{\rho\sigma})_{v^f R^f, v^i R^i} = \langle R^f | \langle v^f | \hat{\alpha}_{\rho\sigma}(Q) | v^i \rangle | R^i \rangle \quad (26)$$

$$\begin{aligned}
\hat{\alpha}_{\rho\sigma}(Q) = & \frac{1}{\hbar} \sum_{r \neq f,i} \left[\frac{\langle e^g | \hat{P}_\sigma | e^r \rangle \langle e^r | \hat{P}_\rho | e^g \rangle}{\omega_{e^r e^g} + \omega_0} \right. \\
& \left. + \frac{\langle e^g | \hat{P}_\rho | e^r \rangle \langle e^r | \hat{P}_\sigma | e^g \rangle}{\omega_{e^r e^g} - \omega_0} \right] \quad (27)
\end{aligned}$$

Next we change our coordinates from the space-fixed axes (ρ, σ) to the molecule-fixed axes (ρ', σ') . The molecule-fixed axes is defined so that $\hat{\alpha}_{\rho'\sigma'}(Q)$ is diagonal and no longer has any angular dependence. This then separates the rotational and vibrational parts of the tensor:

$$(\alpha_{\rho\sigma})_{v^f R^f, v^i R^i} = \langle R^f | l_{\rho\rho'} l_{\sigma\sigma'} | R^i \rangle \langle v^f | \hat{\alpha}_{\rho'\sigma'}(Q) | v^i \rangle \quad (28)$$

where $l_{\rho\rho'}, l_{\sigma\sigma'}$ are directional cosines used in the transformation.

V. PURE VIBRATIONAL TRANSITIONS

A. The Harmonic Approximation

If you do not have any rotational transitions then the first term in eqn. (28) will become one. At this point we can proceed in the same manner as the classical analysis and expand $\hat{\alpha}_{\rho\sigma}$ as a Taylor series (eqn. 3). Doing this and then plugging it back into eqn. (28) gives:

$$(\alpha_{\rho\sigma})_{v^f, v^i} = (\hat{\alpha}_{\rho\sigma})_0 \langle v^f | v^i \rangle + \frac{1}{2} \sum_k \left(\frac{\partial \hat{\alpha}_{\rho\sigma}}{\partial Q_k} \right)_0 \langle v^f | Q_k | v^i \rangle \quad (29)$$

We can now make a harmonic oscillator approximation and write the vibrational wavefunctions as:

$$\phi_{v^j} = \prod_k \phi_{v^j}^k(Q_k) \quad (30)$$

That is the product of harmonic oscillators, one for each normal mode of vibration with quantum number v_k^j . Placing this into eqn. (29):

$$(\alpha_{\rho\sigma})_{v^f, v^i} = (\hat{\alpha}_{\rho\sigma})_0 \prod_k \langle \phi_{v^f}^k | \phi_{v^i}^k \rangle + \frac{1}{2} \sum_k \left(\frac{\partial \hat{\alpha}_{\rho\sigma}}{\partial Q_k} \right)_0 \prod_k \langle \phi_{v^f}^k | Q_k | \phi_{v^i}^k \rangle \quad (31)$$

We can now find what transitions are allowed by looking at the properties of the harmonic oscillator wavefunctions:

$$\langle \phi_{v^f}^k | \phi_{v^i}^k \rangle = \begin{cases} 0 & \text{For } v_k^f \neq v_k^i \\ 1 & \text{For } v_k^f = v_k^i \end{cases} \quad (32)$$

$$\langle \phi_{v^f}^k | Q_k | \phi_{v^i}^k \rangle = \begin{cases} \sqrt{v_k^i + 1} b_{v_k} & \text{For } v_k^f = v_k^i + 1 \\ \sqrt{v_k^i} b_{v_k} & \text{For } v_k^f = v_k^i - 1 \\ 0 & \text{Otherwise} \end{cases} \quad (33)$$

Where

$$b_{v_k} = \sqrt{\frac{\hbar}{2\omega_k}} \quad (34)$$

We now look to see what conditions must be satisfied for the two terms in eqn. (31) to be non-zero. The first term is non-zero only if none of the vibrational quantum numbers change and if $(\hat{\alpha}_{\rho\sigma})_0$ is non-zero. Since not all the components of the equilibrium polarizability tensor can be zero there will always be Rayleigh scattering.

The second term is non-zero if all the terms in the product are non-zero. This means that for the k^{th} mode $v_k^f = v_k^i \pm 1$ and $v_j^f = v_j^i$ for $j \neq k$. A transition of this type gives rise to the Stokes and anti-Stokes lines. In addition to this $\left(\frac{\partial \hat{\alpha}_{\rho\sigma}}{\partial Q_k} \right)_0$ must also be non-zero. No general statement can be made about this term until you know the geometry of the molecule.

B. Vibrational Spectra

For spectroscopy it is more convenient to use the wavenumber, $\tilde{\nu}$, instead of frequency, ω for spectra. Now with the selection rules for vibrational transitions calculated it is straightforward to find what the wavenumber shifts will be for the Raman effect. A negative wavenumber shift ($\tilde{\nu}_0 - |\Delta\tilde{\nu}|$) will give the Stokes line and a positive wavenumber shift ($\tilde{\nu}_0 + |\Delta\tilde{\nu}|$) will give anti-Stokes lines.

The scaled energy of a harmonic oscillator is:

$$G(v) \equiv \frac{E_v}{hc} = (v + 1/2)\tilde{\nu} \quad (35)$$

These energy levels are evenly spaced so the selection rule $\Delta v = \pm 1$ will lead to Raman lines with a wavenumber shift equal to $\tilde{\nu}_k$, the wavenumber of the k^{th} normal mode, for all allowed transitions (see Fig. 3 (a and b)).

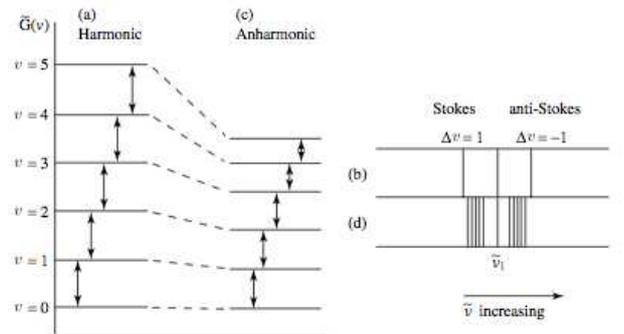


FIG. 3: Vibrational states (a) and Raman spectra (b) for a harmonic oscillator. Vibrational states (c) and Raman spectra (d) for an anharmonic oscillator. Image taken from *The Raman Effect* [3]

For most molecule the vibrational modes are anharmonic. In this case the scaled energy levels look like:

$$G(v) = (v + 1/2)\tilde{\nu}_e - (v + 1/2)^2\tilde{\nu}_e x_e \quad (36)$$

Where $\tilde{\nu}_e$ is the harmonic wavenumber and $x_e \ll 1$. The energy levels are depicted in Fig. 3(c). Now the wavenumber shift for $\Delta v = 1$ is:

$$|\Delta\tilde{\nu}| = \tilde{\nu}_e - 2(v+1)\tilde{\nu}_e x_e \quad (37)$$

And you will get a similar expression for the $\Delta v = -1$ transition as well. Now the wavenumber shift is dependent on the vibrational quantum number meaning the spectra lines will be spread out as depicted in Fig. 3(d).

VI. PURE ROTATIONAL TRANSITIONS

A. Diatomic Molecule

From eqn. (28) it is clear that rotational transitions will arise from the geometry of the molecule. For simplicity we will look at a diatomic molecule. For this case it can be shown that $\alpha_{x'x'} = \alpha_{y'y'} \neq \alpha_{z'z'}$ where $\alpha_{\rho'\sigma'}$ is the second term of eqn. (28) when there is no vibrational transition.

If we take an incoming photon whose electric field makes an angle θ with the bond axis of the molecule then the zz component of eqn. (28) becomes:

$$(\alpha_{zz})_{R^f, R^i} = \langle R^f | \alpha_{x'x'} l_{x'z}^2 + \alpha_{y'y'} l_{y'z}^2 + \alpha_{z'z'} l_{z'z}^2 | R^i \rangle \quad (38)$$

This can be simplified by using the following properties of the directional cosines and the geometry of the system:

$$l_{x'z}^2 + l_{y'z}^2 + l_{z'z}^2 = 1 \quad (39)$$

$$l_{z'z} = \cos(\theta) \quad (40)$$

This leads to:

$$\begin{aligned} (\alpha_{zz})_{R^f, R^i} &= \alpha_{x'x'} \langle R^f | R^i \rangle \\ &+ (\alpha_{z'z'} - \alpha_{x'x'}) \langle R^f | \cos^2(\theta) | R^i \rangle \end{aligned} \quad (41)$$

We also know that the angular wavefunctions have the following properties:

$$\langle R^f | R^i \rangle = 0 \quad (42)$$

Unless $\Delta l = 0$ and $\Delta m = 0$, where l and m are the angular momentum and magnetic quantum numbers, and

$$\langle R^f | \cos^2(\theta) | R^i \rangle = 0 \quad (43)$$

Unless $\Delta l = 0, \pm 2$ and $\Delta m = 0$.

You can also do a similar analysis of the other components of the polarizability tensor and find that the selection rules for l are $\Delta l = 0, \pm 2$ and for m are $\Delta m = 0, \pm 1$

B. Rotational Spectra

We will now assume that our molecule is a rigid rotor. If this is the case then the scaled energy will be (Fig. 4(a)):

$$F(l) \equiv \frac{E_R}{hc} = Bl(l+1) \quad (44)$$

$$B \equiv \frac{h}{8\pi^2 I c} \quad (45)$$

Where I is the moment of inertia about the axis through the center of gravity and about the axis perpendicular to the bond.

Looking at the selection rule $\Delta l = 2$ (called the S branch) the resulting $\Delta\tilde{\nu}_S$ will be:

$$|\Delta\tilde{\nu}_S| = 4B(l+3/2) \quad (46)$$

When $\Delta l = -2$ the transition belongs to the O branch and when $\Delta l = 0$ it belongs to the Q branch. The Raman lines that will result from this will be evenly spaced (Fig. 4(b)). The S and O branches will have and same spacing and the Q branch will have a smaller spacing.

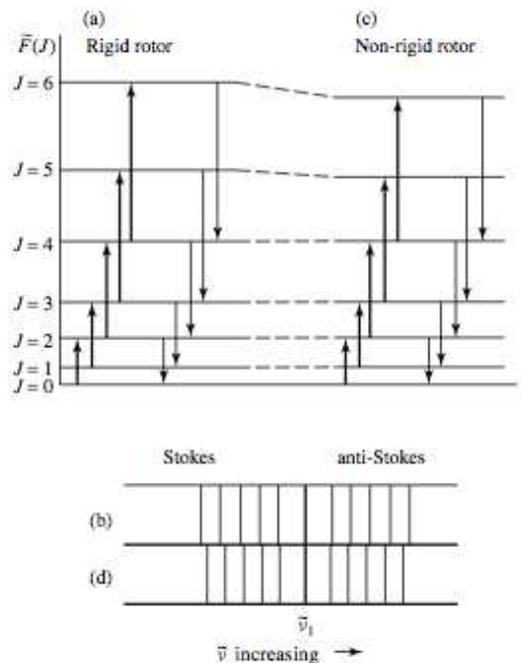


FIG. 4: Rotational states (a) and Raman spectra (b) for a rigid rotor. Rotational states (c) and Raman spectra (d) for a non-rigid rotor. Image taken from *The Raman Effect* [3]

Most molecule are better described by a non-rigid rotor with scaled energy (Fig. 4(c)):

$$F(l) = Bl(l + 1) - Dl^2(l + 1)^2 \quad (47)$$

Where D is the centrifugal stretching constant. Using this the wavenumber shift for the S band be-

comes:

$$|\Delta\tilde{\nu}_S| = (4B - 6D)(l + 3/2) - 8D(l + 3/2)^3 \quad (48)$$

Now the lines no longer have the same spacing, but the spacing gets smaller the farther they are from $\tilde{\nu}_0$ (Fig. 4(d)).

[1] N. B. Colthup, L.H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, 1990.

[2] D. A. Long, *Raman Spectroscopy*, McGraw-Hill In-

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[3] D. A. Long, *The Raman Effect*, John Wiley & Sons Ltd., 2002.