The Wonders of Raman Spectroscopy

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Abstract

The simplest, most common light scattering process is that of Rayleigh scattering. In this case an incident photon, of frequency v_0, is absorbed by an atom or molecule—pumping it up to an excited electronic state. This will be an unstable configuration, and the atom or molecule will decay back to the original state—releasing a photon of identical frequency as that of the incident photon. Since the incident and emitted photons have the same energy (frequency), Rayleigh scattering is an elastic process. In contrast, Raman scattering is an inelastic process, arising from transitions between adjacent vibrational levels of a molecule. When a sample is illuminated by a laser beam, both Rayleigh scattering and the much weaker Raman scattering occur. The intensity of the Raman scattered light is ~10^{-5} to 10^{-6} of the incident beam [1, 2, 3]. This Raman scattering consists of frequencies $v_0 \pm v_{vib}$, where v_{vib} is the frequency of some vibration of the molecule. Thus, what is observed in Raman spectroscopy are two separate peaks: the Stokes $(v_0 - v_{vib})$ and anti-Stokes $(v_0 + v_{vib})$ peaks. Raman spectroscopy measures the vibrational frequency v_{vib} as a *shift* away from the incident frequency v_0. This methodology has been extensively used on organic and inorganic systems. We will explore how Raman spectroscopy, unlike spectroscopic systems such as FTIR (Fourier

Transform Infrared Spectroscopy), enables observations of both vibrational features as well as defects, therefore allowing identification of nanoscale structures and bonding in selenium, tellurium, and nanotubes.

Introduction

Raman scattering is an inelastic process, arising from transitions between adjacent vibrational levels of a molecule. When the sample is illuminated by a laser beam, both types of scattered light occur—the typical Rayleigh scattering, and the much weaker Raman scattering. Raman scattering consists of frequencies v_0 and v_{vib}, where v_{vib} is the frequency of some vibration of the molecule. Thus, what is observed in Raman spectroscopy are two separate peaks: the Stokes $(v_0 - v_{vib})$ and anti- Stokes $(v_0 + v_{vib})$ peaks. Therefore, what is measured in Raman spectroscopy is the vibrational frequency v_{vib} as a *shift* away from the incident frequency v_0. Because the anti-Stokes peaks are so much weaker than the Stokes peaks, in practice usually only the Stokes peaks are measured [1, 2, 3].

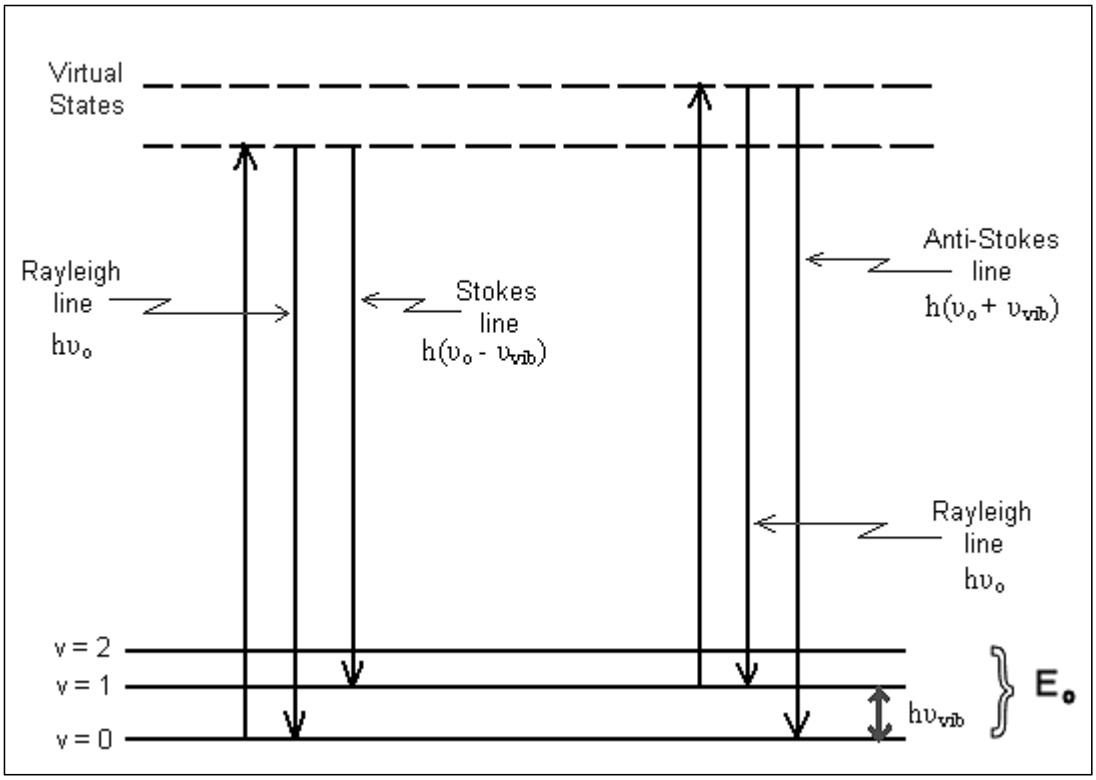

Figure 1.1: Energy level diagram showing Stokes and Anti-Stokes Raman scattering, and Rayleigh scattering [4].

In Figure 1.1, above, v = 0 through v = 2 denote three different vibrational levels which all belong to the ground electronic state, denoted as E_0. As can be seen from Figure 1.1, for the Stokes line, the molecule ends up in a higher (vibrational) energy state than it was initially. Whereas for the anti-Stokes line to occur, it is necessary for the molecule to be in an excited vibrational state to begin with before the photon scattering process occurs. In this case, the molecule is in a lower energy vibrational state after the scattering process [2, 5].

It should also be emphasized that the dashed lines in the Figure are purely *virtual* states. The only condition necessary for Raman scattering is that the energy hv_0 of the incident photon must be greater than the energy difference, $\Delta E = hv_{vib}$ between the final and initial states of the *actual* vibrational transition[1]. Since no *actual* transition takes place to any given virtual state, v_0 is not matched to any absorption frequency of the scattering molecule [2, 5]. The anti-Stokes line is much weaker in intensity than the Stokes line—since typically the v=1 level will be much less populated than the v=0 level. This can be seen using the Maxwell-Boltzmann distribution:

$$\frac{P(v=1)}{P(v=0)} = e^{\frac{-\Delta E}{kT}} \qquad (1)$$

where P(v=1) and P(v=0) are the populations of the v=1 and v=0 vibrational levels (respectively) [1, 2, 6, 7]. Here, ΔE is the energy difference between these levels, k is Boltzmann's constant, and T is the absolute temperature. This ratio will become smaller as ΔE increases and/or T decreases—and as this ratio shrinks, the anti-Stokes line will become increasingly less intense compared to the Stokes line. A simplified analysis of Raman scattering can be obtained using classical wave theory. The typical treatment is as follows [1]: if the

molecule is irradiated by a laser with frequency v_0, then the electric field strength of this electromagnetic wave varies in time as:

$$E = E_0 \cos(2\pi v_0 t) \tag{1.1}$$

For a simple diatomic molecule, this induces an electric dipole moment (P) given by [1]

$$P = \alpha E_0 = \alpha E_0 \cos(2\pi v_0 t) \tag{1.2}$$

where α is the polarizability of the molecule. Now if the molecule itself is vibrating where q is a generalized coordinate for the nuclear displacement (i.e. $r - r_o$, where r is the nuclear separation and r_o is the equilibrium nuclear separation), and q_o is the amplitude of this vibration [1], polarizability, α, is itself a function of this nuclear displacement. However, for small amplitude vibrations, it is possible to use a Taylor expansion for α about the equilibrium point, and drop any terms that are higher than first order in the amplitude of vibration q_1

$$\alpha = \alpha_0 + \left[\frac{\delta\alpha}{\delta q}\right] + \cdots \tag{1.3}$$

In the equation α_o is the polarizability at the equilibrium position, and $\left[\frac{\delta\alpha}{\delta q}\right]$ is the rate of change of α with respect to q, evaluated at the equilibrium position [1]. Substituting this expression for α into the equation for P yields:

$$P = \alpha_0 E_0 \cos(2\pi v_0 t) + q E_0 \left[\frac{\delta\alpha}{\delta q}\right] \cos(2\pi v_0 t) \tag{1.4}$$

Next, the expression for the nuclear displacement is substituted into equation P to obtain [1]:

$$P = \alpha_0 E_0 \cos(2\pi v_0 t) + \left[\frac{\delta\alpha}{\delta q}\right]_n q_0 E_0 \cos(2\pi v_0 t) \cos(2\pi v_m t) \tag{1.5}$$

Finally, using the fact that $\cos(x)\cos(y) = \frac{1}{2}[\cos(x+y) + \cos(x-y)]$, the induced electric dipole moment, P, takes the form:

$$P = \alpha_0 E_0 \cos(2\pi v_0 t) + \frac{1}{2}\left[\frac{\delta\alpha}{\delta q}\right]_n \{\cos[2\pi(v_0 + v_m)t] + \cos[2\pi(v_0 - v_m)t]\} \qquad (1.6)$$

From equation 1.6, we see that the first term is an oscillating dipole which is radiating at frequency v_0—the same frequency as the incident light [1]. Thus, this term corresponds to Rayleigh scattering. The second term represents the Raman scattering with two different frequencies — $(v_0 - r_m)$ corresponding to the Stokes line, and $(v_0 + v_m)$ corresponding to the anti-Stokes line [1]. This Equation also makes it obvious that for a vibration to be Raman active $(\frac{\delta\alpha}{\delta q})_n$ must be non-zero. The Stokes lines are more intense than the anti-Stokes lines—but they both provide the same information [2, 3, 4, 6]. So, in practice, only the Stokes side of the spectrum is actually measured [2, 5]. A simplified quantum mechanical analogue can also illustrate the differences between Rayleigh and Raman scattering. In this case, the vibrational transition moments must be considered.

$$P_{nm} = \alpha_{nm} E = E\left[\int \psi_n^* \alpha \psi_m \delta q\right] \qquad (2.0)$$

where, as before, α is considered to be a function only of the nuclear vibrational (displacement) coordinate, ψ_m and ψ_n are the vibrational wave functions of the two vibrational states, and α_{nm} is the quantum mechanical analogue of the polarizability [1, 5, 9]. Substituting in the same Taylor expansion (for α) as before, gives α for a vibrational transition n → m [5]:

$$= a_{nm} = \left[\int \psi_n^* \alpha \psi_m\right] \delta q \qquad (2.1)$$

$$= \int \psi_m \alpha_0 \psi_n + \int \psi_m^* \left[\frac{\delta\alpha}{\delta q}\right] \int \psi_n \delta q \tag{2.2}$$

Note that a_0 and $(\frac{\delta\alpha}{\delta q})_0$ are constants and can be pulled outside of the integrals, resulting in:

$$\alpha_{nm} = \alpha_0 \int \psi_m^* \psi_n dq + \left(\frac{\delta\alpha}{\delta q}\right)_0 \int \psi_m^* \psi_n dq \tag{2.3}$$

The first integral in equation 2.3 above vanishes unless n = m due to the orthogonality of the wave functions. If only simple harmonic vibration is considered, then the vibrational wave functions are harmonic oscillator wave functions, and thus the second integral vanishes unless m = n ± 1 [5, 9]. Therefore, if n = m (i.e. no vibrational transition takes place) the second integral vanishes, leaving only the first integral in the above equation corresponding to Rayleigh scattering. However, if m = n ± 1, (a vibrational transition does occur) then the first integral vanishes, while the second integral remains, corresponding to Raman scattering. This equation also illustrates that $(\frac{\delta\alpha}{\delta q})_0$ must be non-zero [1].

The previous discussion for the induced electric dipole moment was simplified by discussing it in terms of a simple model of a diatomic molecule, starting with P = αE, assuming that E was oriented along the axis of the diatomic molecule, and also assuming that the induced dipole moment was along the axis of the diatomic molecule (i.e. a completely one-dimensional treatment). However, in real molecules the situation is more complex, since P and E are both vectors consisting of three components each (x, y, z). Therefore, the components of P must be written as [2, 3, 4, 6, 9]:

$$P_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z \tag{2.4}$$

$$P_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z \tag{2.5}$$

$$P_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z \tag{2.6}$$

Now, the polarizability is no longer just a constant, but rather the first matrix on the right- hand side, called the *polarizability tensor*. In normal Raman scattering this is a symmetric tensor—meaning $\alpha_{xy} = \alpha_{yx}$, etc. [1, 2, 3, 5, 6] In this case, for a vibration to be Raman active, at least *one* component of the polarizability tensor must change during a vibration [1, 2, 4]. Since the polarizability is a tensor, each component must be included in the previous treatment. For instance, previously α was expanded about the equilibrium position, now that tensor must be written as:

$$\alpha_{ij} = \alpha_{ij} + \left(\frac{\delta\alpha_{ij}}{\delta q}\right) q + \cdots \tag{3.0}$$

where α_{ij} refers to the ith, jth component of the polarizability tensor, and $(\alpha_{ij})_0$ is α_{ij} at the equilibrium position [3, 8]. However, this is still extremely simplified and valid only for a diatomic molecule since it is considering only *one* normal coordinate (nuclear displacement), q, into consideration. The Taylor expansion, to first order in q, should really be written as [3]:

$$\alpha_y = (\alpha_{ij}) + \sum \kappa \left(\frac{\delta\alpha_{ij}}{\delta q_k}\right) q_k + \tag{3.2}$$

where $(\alpha_{ij})_0$ is the same as before, q_k are the various vibrational normal coordinates of vibration, and the summation is taken over *all* possible normal coordinates. In this case, Raman activity is predicted by the *derived* polarizability tensor:

$$\alpha_{ij} = \frac{\delta\alpha_{ij}}{\delta q_k} \tag{3.3}$$

Raman scattering will occur as long as the derivative (taken at the equilibrium position) of at least one component of the polarizability tensor, with respect to some vibrational normal coordinate is non-zero [3]. It was previously stated that a normal mode of vibration will be Raman-active if some component of the polarizability tensor (or derived

polarizability tensor) changes during the vibration. If one were to plot α_i (α in the i-direction) from the center of mass in all directions, a 3-dimensional surface would be obtained. However, by convention, people typically plot $\frac{1}{(\alpha_i)^{\frac{1}{2}}}$ and name the resulting 3-dimensional body the polarizability ellipsoid [1, 2, 3, 6].

The Raman activity of a vibration can be considered in terms of this polarizability ellipsoid. A vibration will be Raman-active if the size, shape, or orientation of the polarizability ellipsoid changes during the normal vibration [2, 6]. It is instructive to consider these ellipsoids for a couple simple molecules, such as CO_2 and H_2O. Figure 1.2, below, shows the polarizability ellipsoids for the normal vibrations of a CO_2 molecule. As can be seen in Figure 1.2, for the ν1 vibration, the *size* of the ellipsoid is changing. This means that the diagonal elements $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$ are changing simultaneously. Therefore, this vibration is Raman-active.

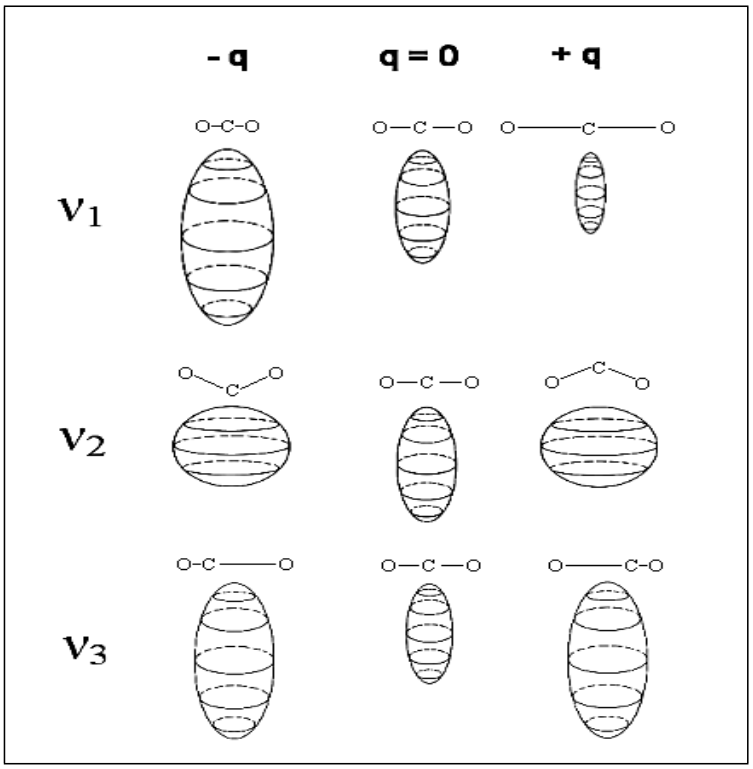

Figure 1.2: Polarizability ellipsoids for the normal vibrations of a CO2 molecule [2].

However, neither the ν2 nor the ν3 vibrations are Raman active. In the ν2 mode, the *shape* of the ellipsoid is changing, and for the ν3 mode, the *size* of the ellipsoid is changing. However, for both the ν2 and the ν3 vibrations, the polarizability ellipsoids are the same at the two extreme displacements (+q and –q). Therefore, since Raman is determined by whether or not the slope near the equilibrium point, $(\frac{\delta\alpha}{\delta q})_n$ is non-zero, neither ν2 nor ν3 vibrations are Raman active if a small displacement about equilibrium is considered [2]. Shown in Figure 1.3, a qualitative graphical depiction (for the CO_2 molecule) of how a component of the polarizability, α, varies with respect to the nuclear displacement, q.

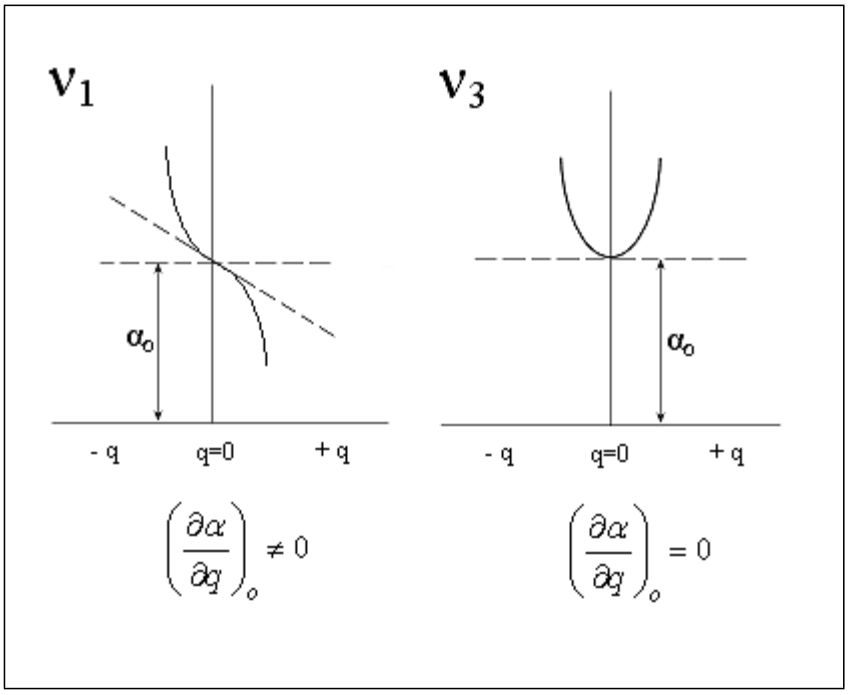

Figure 1.3: Differences between the polarizability of the v1 and v3 normal vibrations of a CO_2 molecule [1, 2].

From Figure 1.3, it is easy to see that for the ν_1 vibration, the slope, $(\frac{\delta\alpha}{\delta q})_n$, is non-zero at the equilibrium point (q = 0), and thus the vibration is Raman-active. However, for the ν_3 vibration, the slope, $(\frac{\delta\alpha}{\delta q})_n$ is equal to zero at the equilibrium point, meaning this vibration is not Raman-active [2].

The H_2O molecule is exactly analogous to the v_1 vibration for the CO_2 molecule, in that the size Figure 1.4, below, depicts the polarizability ellipsoids for the three normal vibrations of an H_2O molecule. In this case, all three vibrations are Raman-active [1]. The v_1 vibration is changing, and is different at the two extremes, +q and –q. The v_2 vibration is Raman-active because the shape is changing and is different at the two extreme configurations. This means that the diagonal elements of the polarizability tensor are changing simultaneously, but at different rates. For the v_3 vibration, the *orientation* of the ellipsoid is changing and is different at the two extremes.

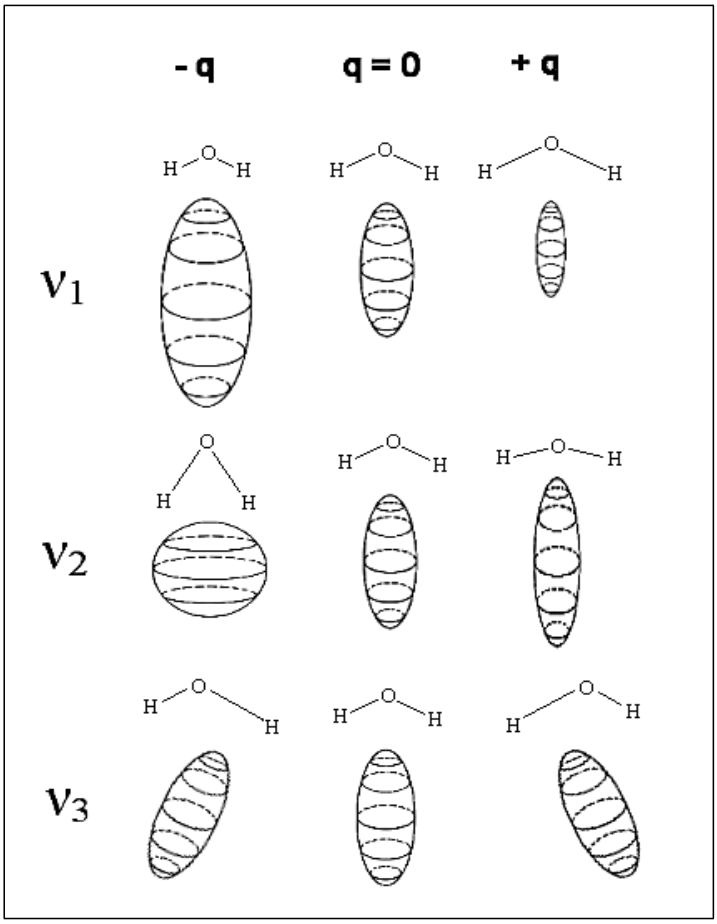

Figure 1.4: Polarizability ellipsoids for the normal vibrations of an H2O molecule [1, 2].

This corresponds to a change in an off-diagonal element of the polarizability tensor, which means this vibration is also Raman-active [2]. These examples show that for determining

Raman activity, it is not necessary to determine the exact (quantitative) nature of the ellipsoid, but rather the qualitative nature of how the ellipsoid changes during a normal vibration. However, while this simple approach gives some graphical insight into whether a normal vibration is Raman active, it is not valid for larger, more complex molecules [14].

Results and Discussion

The use of visible RRS for analyzing carotenoids in biological matrices, for pigments and dyes as dealt with in art and forensics; (2) The use of RRS in the deep UV (excitation below 260 nm) in the bio-analytical and life sciences fields, including nucleic acids, proteins and protein–drug interactions; and (3) Metalloproteins can be studied by visible RRS in resonance with their chromophoric absorption. The selective enhancement of the Raman scattering from specific modes under resonance conditions means that RRS is especially useful to distinguish mixtures of complex nanomaterials. One of the best examples to illustrate the use of RRS is to analyze single-walled carbon nanotubes (SWCNTs). SWCNTs can be seen as a rolled-up sheet of a single layer of graphene, seamlessly fused and with a typical diameter of about few nm. The length is often orders of magnitude greater. Many properties of SWNCTs, for instance whether they are semi-conductive or metallic, are related to the diameter and chirality angle, usually given by the indices (n, m). SWCNTs are produced as mixtures with a distribution of (n, m) values and it is very difficult to distinguish each species using conventional analytical instruments. Fortunately, SWCNTs have strong, narrow absorption features in the visible and near-IR range, the maxima depending on the (n, m) indices. Tuning the laser to these narrow absorption bands can provide enormous selectivity in RRS. Studies have shown that excitation-emission matrices that showed sharp Raman spectra at different excitation frequencies. The radial breathing modes (RBMs) in the 100 – 400 cm^{-1} range are useful to identify the geometry of the compound. Based on theoretical considerations and comparisons with absorption and luminescence data RRS cross

sections are derived, the relative abundance (metallic/semi-conductive) of the different species in the sample can be estimated [3]. Studies have also shown that defects of multi-walled carbon nanotubes (MWCNTs) can be examined through the D/D' modes using RRS [4].

In 1994 published Raman spectra analysis of 1st and 2nd order spectra was presented in Chem Phys Lett, one of the first efforts to look at the higher 'graphitic' modes and was part of the PhD thesis from Curran (1995). These modes show differences between HOPG and amorphous carbon. Associated line at 1350 cm^{-1} with disorder similar to graphite, but the height and full width half max (FWHM) purity of the nanotubes in place. The larger the height and broader the spectrum the greater the impurities and less nanotubes present. The line at 1580 cm^{-1} is associated with the E2g G mode or the 'graphitic mode, one we see mainly in HOPG, Nanotubes and graphene. The assigned line at 2700 cm $^{-1}$ as second order Defect (D) line but its spacing is more to do with interactions in terms of bonding to the nanotubes. We now know E2g mode at 1578 cm $^{-1}$ is composed of longitudinal and transverse G modes at 1575 cm $^{-1}$ and 1584 cm $^{-1}$. We know that the D+G mode is found at 2930 cm $^{-1}$ which is a combination of graphitic states and defective states.

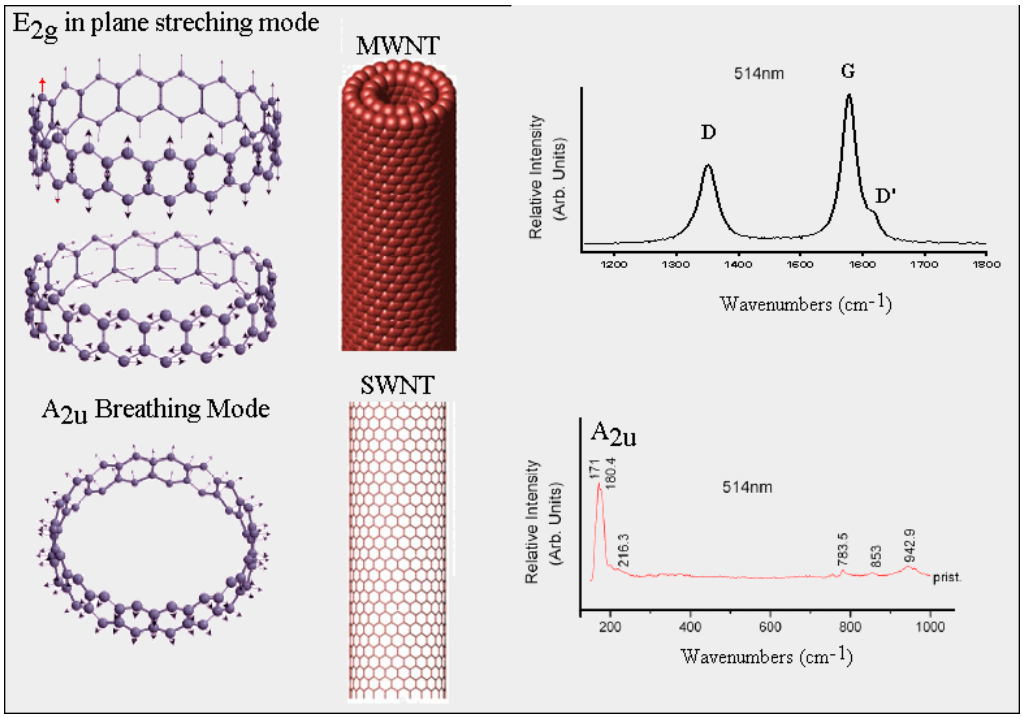

Figure 1.5: Shown on the top right is a depiction of the graphitic mode [G], defect states [D], and bonding states [D']. On the bottom right is the first breathing mode of a nanotube.

These defects are specific to two areas that need to be defined, functionalization and disorder functionalization, changing the graphitization to increase reactivity of nanotubes. Disorder: Amorphous carbon, pentagon and heptagon rings, breaks in conjugation along tube body, strain in C=C bonds and can be the cause of different hybridizations.

Conclusion

Raman Spectroscopy is a very powerful analytical tool used to reveal the nature of vibrational / rotational transitions and low frequency modes in liquid, gaseous and solid samples such as molecules, crystals, powders, and biological media. Analysis of Raman spectra can yield information on the bonding, structure, symmetry and even electronic transitions between ground states and low-lying excited energy states when carrying out resonance Raman spectroscopy. In general, the spectra recorded for Raman spectroscopy are displayed as a shift from the incident beam frequency. When taking spectra, it is best to use low power and longer

integration time to prevent false information generate displaying false carbon based defect signals. Raman Spectroscopy (RS) is based on the inelastic scattering of radiation in the visible or near-infrared region by a sample. Usually the largest fraction of the scattered light has the same wavelength as the laser light (Rayleigh scattering). However, in the most common form of Raman scattering (Stokes Raman), weak scattered light at longer wavelengths is also observed, where its photon energy is reduced by a vibrational energy quantum of the scattering molecule. Therefore, RS is a vibrational spectroscopic technique—complementary to Infrared (IR) spectroscopy—but excitation and emission involve higher-energy photons, similar to those used in electronic absorption and fluorescence spectroscopy. Resonance Raman Spectroscopy (RRS) is an extension of conventional RS that can provide increased sensitivity to specific compounds that are present at low (micro- to milli-molar) in an otherwise complex mixture of compounds. Normally Raman emission is rather weak, but it can be enhanced by several orders of magnitude in the special situation where the laser wavelength is close to an electronic absorption band (resonance). The smaller the difference in frequency between laser and electronic transition, the stronger is the RRS intensity. In practice of RRS, the wavelength of the incoming laser is selected to coincide with an electronic transition of the materials of interest. Because the energy of electronic transitions varies widely from material to material, wavelength-tunable lasers (Argon and Krypton ion) are usually used to coincide with an electronic transition (resonance). The vibrational modes that undergo a change in bond length/force constant during the electronic excitation can show a large increase in polarizability and hence Raman intensity. The increase can be by a factor of 10 to > 100,000 and is most apparent in the case of π-π^* transitions. In terms of chemical analyses of unknown compounds, the main advantage of RRS over conventional RS is the large increase in intensity of the bands in question (by as much as a factor of 10^6). This allows resonance Raman spectra to be obtained with sample concentrations as low as 10^{-8} M. This is in stark contrast to conventional Raman spectra, which usually requires

concentrations greater than 0.01 M. Resonance Raman spectra usually exhibit fewer bands than the conventional Raman spectra of a compound, and the enhancement seen for each band can vary depending on the electronic transitions with which the laser is resonant.

Acknowledgements

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