

Raman Spectroscopy: Basic Principles, Techniques, and One (of many) Applications

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1 Introduction

Raman Spectroscopy, in its most general classification, is a form of vibrational spectroscopy, which involves emission and absorption of infrared (IR) and visible light (as the form of light-based interaction with the molecule). Specifically, Raman spectroscopy is concerned with the latter, the absorption and emission of visible light; moreover, unlike Rayleigh scattering (the frequency invariant phenomenon which makes the sky blue), Raman scattering requires a change in frequency; hence, it is actually the inelastic scattering of light.

Note the difference between Stokes, Anti-Stokes, and Rayleigh scattering as seen in Figure 1. The first two are phenomena of Raman scattering to be described below.

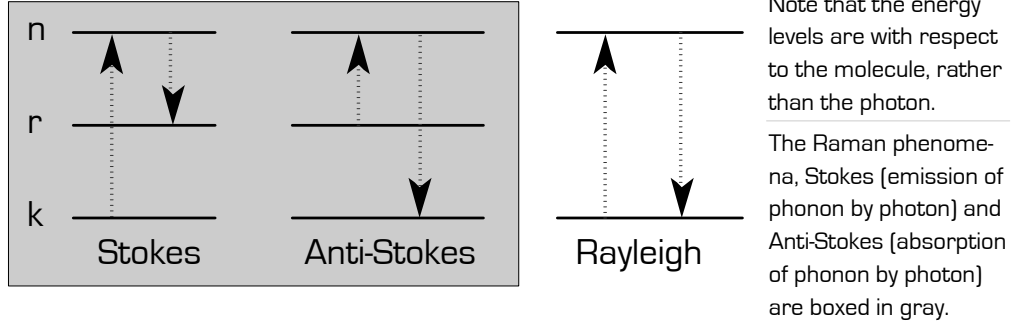
With the exception of studying gases, Raman by far outdoes IR, Proton NMR, mass, and UV spectroscopy. As can be seen in Figure 2, Raman's only defect is its relative pricing.

A close cousin of Raman would be IR. In some respects, they are complements of each other, as there are certain studies where Raman may discern data IR cannot and vice versa. In general, this would be based on the difference in the two methods - mainly, Raman can detect changes that do not involve dipole moment. However, pricing is again a factor, as Raman's price range is right above that of IR.

2 Principles

Consider an incident photon against a molecule. This interaction either involves the absorption or emission of a phonon. Thus, two conservation equations immediately arise:

Figure 1: Raman vs Rayleigh. Modified from [1]



$$E_{initial} = E_{final} \implies \hbar\omega \pm \hbar\omega(\vec{k}) = \hbar\omega' \quad (1)$$

$$\vec{p}_{initial} = \vec{p}_{final} \implies \hbar n\vec{q} \pm \hbar\vec{k} + \hbar\vec{G} = \hbar n\vec{q}' \quad (2)$$

where \vec{G} is the reciprocal lattice vector and primes denote the final frequency (ω') and the final photon wave vector (\vec{q}'), respectively, while $\hbar\vec{k}$ can be regarded as a quasi-momentum, as befits phonons, and according to the eigenvalue of the momentum operator in the position basis (recall: $\vec{p} = -i\hbar\nabla \Rightarrow \vec{p}\psi = \hbar\vec{k}\psi$ where $\psi \propto e^{i\vec{k}\cdot\vec{r}}$).

One can derive an expression for \vec{k} from either phonon absorption (anti-Stokes) or phonon emission (Stokes).

$$k/2 = nq' \sin(\theta/2) = nq \sin(\theta/2) = \frac{\omega}{c} n \sin(\theta/2) \quad (3)$$

Note that since the frequency change in photons is negligible, relative to the magnitude of \vec{k} the vector diagram (c.f., figure 3) can be approximated as a geometrical isosceles triangle. Also, as usual: $q = \omega/c$. Note that the same result can be derived from a wave view of the phenomenon. The derivation is omitted for brevity.

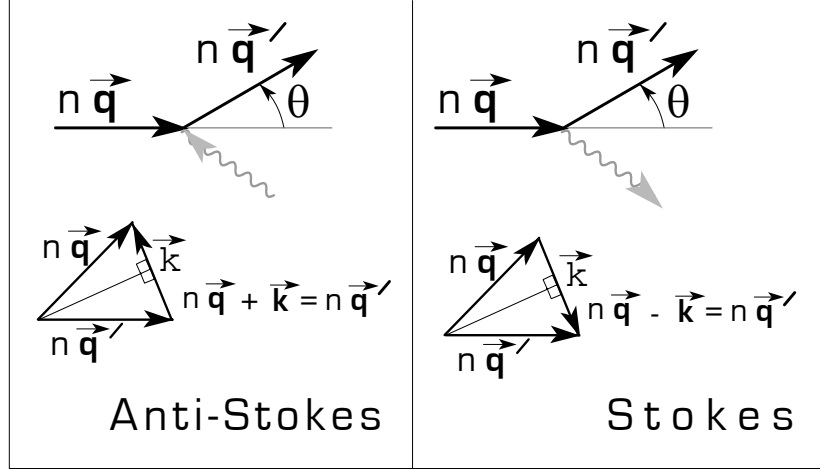
More specifically, the Raman effect is the result of a double transition involving three stationary levels, i.e., the Raman line from an initial level k to a final level n can only occur if there is an intermediate level r . (See Figure ??.) This intermediate quantity has no influence on Raman Scattering.

As a brief aside, recall from Electrodynamics that the basic theory of light scattering rests on the fact that the incident light wave induces an oscillating dipole moment in the molecule ($\vec{\mu} = \alpha_{ij}\vec{E}_0 \cos(2\pi\nu t)$) where α_{ij} is the polarizability tensor. The Raman transition is allowed and the line has an appreciable intensity if at least one of the six independent components of α_{ij} is non-zero.

Figure 2: Comparison of Spectral Disciplines. Modified from [3]

TECH	min sample size [g]	powders	single crystals	neat liquids	aqueous solutions	gases	polymer fibers	fingerprint	general analysis	approx. price (\$)
raman	10^{-6}	very simple	very simple	very simple	very simple	difficult	simple	excellent	excellent	15,000 - 25,000
infrared	10^{-6}	simple	very difficult	very simple	difficult	simple	very difficult	excellent	excellent	7,000 - 15,000
p-NMR	10^{-5}	not possible	not possible	simple	very simple	very difficult	very difficult	fair	excellent	20,000
mass	10^{-10}	not possible	not possible	very simple	difficult	very simple	not possible	good	good	40,000
UV	10^{-6}	not possible	not possible	very simple	very simple	simple	not possible	poor	poor	5,000 - 12,000

Figure 3: Vectoral Diagrams of Anti/Stokes Phenomenon. Modified from [4]



Specifically, unlike IR, which requires change in dipole moment, Raman requires change in the polarizability of the molecule (according to its vibration).

As seen in the polarizability ellipsoid diagram in Figure 4, where $C0_2$ is used as a prototypical molecule, deviation in polarizability from equilibrium allows for Raman. Note that certain dipole changes cannot be detected by Raman, as shown by the non-changing polarizability ellipsoids, specifically the non-symmetric and bending ones shown on the bottom part of the figure. (Only the initial and final stages are shown, and the intermediate stage is omitted.) IR would be a good complement for those cases.

Also, further selection rules can be deduced via group theory. For brevity, that bit shall be omitted.

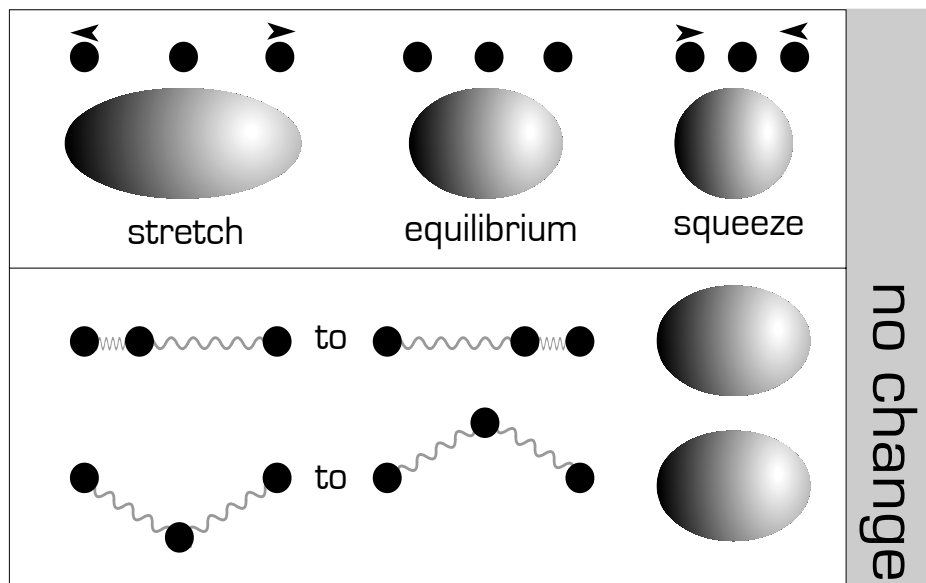
From Raman analysis, one should observe, in general, intensity varying according to ν^4 (except when local to absorption band):

$$\frac{I_a}{I_s} = \left(\frac{\nu + \nu_{vib}}{\nu - \nu_{vib}} \right)^4 \exp\left(\frac{-h\nu_{vib}}{kT} \right) \quad (4)$$

where ν_{vib} denotes the frequency of the molecule and the ν without subscripts denotes the frequency of the light and where I_a , I_s denotes the intensity of the Anti-Stokes and Stokes phenomenon, respectively. The intensity ratio is actually equal to the ratio of population of states in a Boltzmann distribution.

Note that experimentally, only the Stokes phenomenon is observed in the Raman spectrum. However, according to the relation above, the Anti-Stokes phenomenon can be deduced.

Figure 4: Polarizability (Modified from [1] and [3])



3 Techniques

Sir Chandrasekhra Venkata Raman used sunlight as a source, a telescope as the collector, and his eyes as the detector [2]. This was in 1928. Since then, much has evolved; moreover, accuracy and precision seem to have increased multifold with the invention of the laser — (as yet) the ultimate source of adequately intense monochromatic light.

Despite advances in technology, however, the general form of the technique still requires three items:

- a source of illumination, preferably monochromatic light, yielding at least 1 line spectrum
- a container for the substance (not necessary for solid crystals)
- a spectrograph for recording

A proper design of a Raman system requires consideration of factors governing intensity and distribution of Raman scattered radiation. (Recall that the Raman scattered light from a sample is proportional to ν^4 and the intensity of the exciting light.)

Obviously, the ideal Raman illumination system would consist of a geometrical arrangement capable of illuminating a concentrated sample via an intense

light source (λ as short as possible). For non-resonance scattering, the ν must be less than the forbidden electronic energy gap of the sample. The system should also decrease the Rayleigh scattering radiation, as with any incident beam both Rayleigh and Raman are present, usually with $I_{Raman} \ll I_{Rayleigh}$.

Prior to lasers, the cooled-mercury arc lamps were the most intense and monochromatic, providing its most intense lines at 2537, 4046, 4358, 5461 Å. Since the 2537 line arises from resonance transition, the Rayleigh line can be easily eliminated by absorption in a Hg-vapor cell.

With the advent of lasers in the 1960s, Raman spectroscopy received the following advantages:

1. increased variety of exciting lines available with clean spectral region on each side of exciting line
2. bandwidth of laser line usually smaller than that of vapor arc (precision)
3. polarization of laser beam well-defined and well-controlled
4. energy is concentrated in narrow beam
5. intensity may be controlled

The most commonly used lasers for Raman excitation ([6]) are the continuously operating He-Ne (6328 Å) and the Ar-ion (4880, 5145, 4765 Å) gas lasers, and the pulsed and continuously operating forms of the ruby, $Al_2O_3 : Cr^{+++}$ (6943 Å) and the neodymium doped yttrium-aluminum garnet, Nd:YAG (1.06 μ) lasers.

4 Application

Raman can be used to study pretty much all of the material mentioned in Figure ??.

This paper will focus on one application in the food industry. As indicated on the cover page, Raman is almost Ramen. For undergrads and some graduate students, Ramen — non-coherent noodles boiled in oil to maintain flavor and then dried — is essentially a staple food. Using a FT-Raman spectrometer via a Nd:YAG laser source operating at 100-500 mW, it was deduced that the iodine number¹ of the lipid-containing-foodstuff could be estimated using FT-Raman spectra. The presence of double bonds in the unsaturated fatty acids in lipids provides a method of determining unsaturation: the higher the iodine number, the greater the unsaturation. [2]

This paper ends with diagrams of the Raman spectra of the following lipid-containing material: a) sunflower oil; b) corn oil; c) sesame oil; d) rapeseed oil; e) olive oils; f) peanut oil; g) beef tallow; h) butter

¹the related molar ratio measured with respect to each double bond of the unsaturated fatty acid; two iodine atoms per double-bond

Figure 5: Iodine Value of Fatty Acid Foodstuff. Modified from [2]

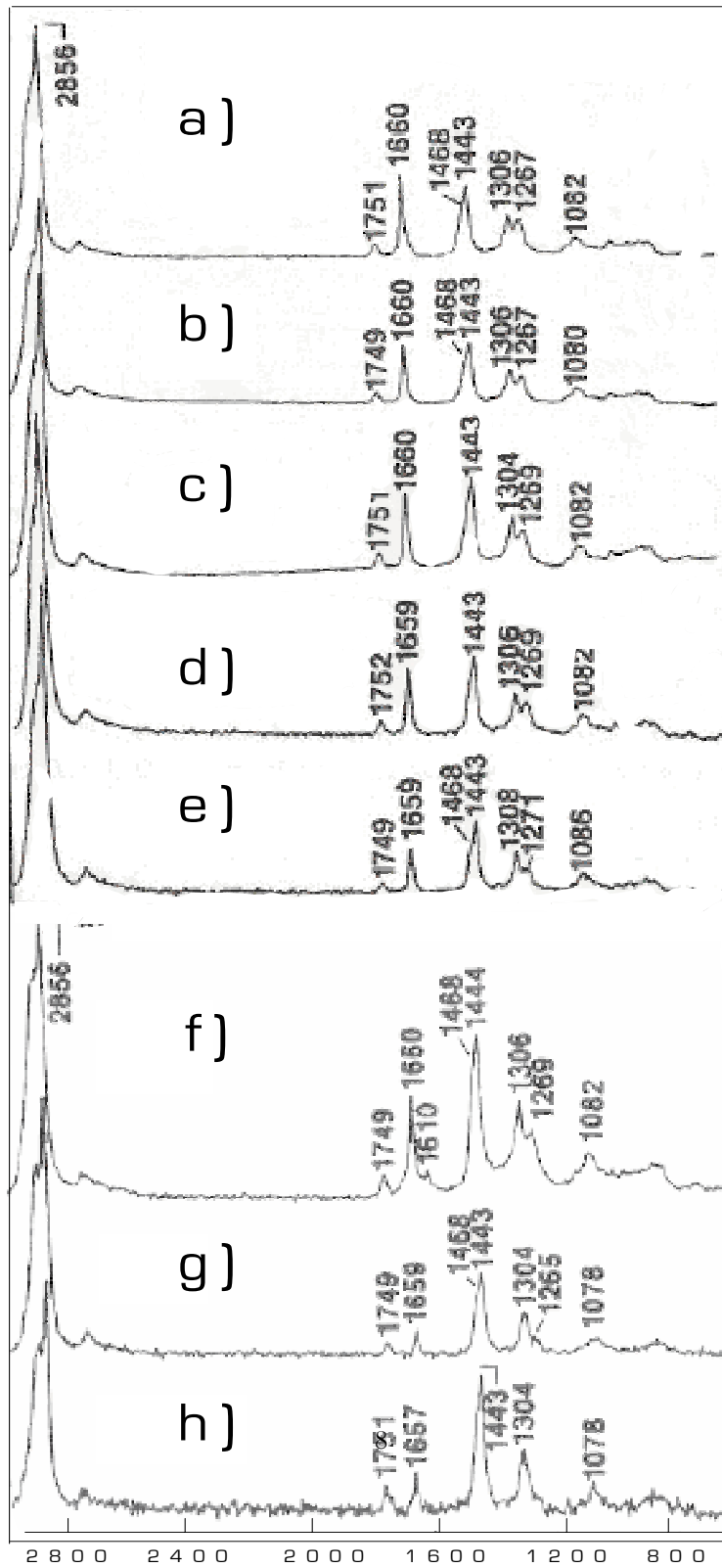
fatty acid compound	iodine value
sunflower oil	136
corn oil	118
sesame oil	111
rapeseed oil	102
olive oil	83
peanut oil	96
beef tallow	40
butter	31

Following this, is a chart containing numerical values of results from Raman analysis. As can be deduced, sunflower oil is the most unsaturated, while butter the least unsaturated. Thus, to preserve the health of undergraduate and graduate students, the dried noodles known as Ramen should be fried in sunflower oil, more so than any of the other compounds.

5 Appendix 1: A More Solid Application

The author chose to do a paper on Raman Spectroscopy primarily because of its practical application above, (especially because of its characteristic “punniness”). However, apparently that application is not so directly related to Solid State Physics, and thus does not fully meet one of the criterion of the paper. Yet, the author is short on time and must concoct a solid summary in about five minutes. Here goes:

Interestingly, Raman has been used to study the compressibility of solids. [2]



expounds upon using $TbVO_4$ and $DyVO_4$. Via correlating bond length deduced from Raman data involving VO stretching frequency to the size of the unit cell of the crystal, one can determine the change in volume of the crystal. For the lanthanide vanadates, a relationship between the volume of the unit cell (VO) and the VO bond distance : VO :

$$V(P) = C : D(VO)_P :^3 \quad (5)$$

The relative value $V(P)/V(0)$ is given by:

$$V(P)/V(0) =: D(VO)_P :^3 / : D(VO)_0 : \quad (6)$$

Compressibility of the V can be estimated if VO bond lengths can be determined as a function of pressure via Raman:

$$\nu_1(A_g) = 21,349 \exp(-1.9176R) \quad (7)$$

The relevant data that is generated from the equations above are listed on page 261 of [2]. For further information, the reader is encouraged to check out the items listed in the bibliography below.

References

- [1] Anderson, L. G. Raman Spectroscopy. Colorado University, Denver. <http://carbon.cudenver.edu/public/chemistry/classes/chem4538/raman.htm>
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- [6] Anderson, A. (Ed). *Raman Effect, The*. Dekker. New York 1971.
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