Raman Spectroscopy

Raman Selection Rules and Intensities

A simple classical electromagnetic field description of Raman spectroscopy can be used to explain many of the important features of Raman band intensities. The dipole moment, P, induced in a molecule by an external electric field, E, is proportional to the field as shown in equation below.

$$P = \alpha E$$

The proportionality constant **α** is the polarizability of the molecule. The polarizability measures the ease with which the electron cloud around a molecule can be distorted. The induced dipole emits or scatters light at the optical frequency of the incident light wave. Raman scattering occurs because a molecular vibration can change the polarizability. The change is described by the polarizability derivative, where **Q** is the normal coordinate of the vibration. The selection rule for a Raman-active vibration, that there be a change in polarizability during the vibration, is given in equation below.

$$\frac{\delta \alpha}{\delta Q} \neq 0$$

The Raman selection rule is analogous to the more familiar selection rule for an infrared-active vibration, which states that there must be a net change in permanent dipole moment during the vibration. From group theory it is straightforward to show that if a molecule has a center of symmetry, vibrations which are Raman-active will be silent in the infrared, and vice versa.

Scattering intensity is proportional to the square of the induced dipole moment, that is to the square of the polarizability derivative. If a vibration does not greatly change the polarizability, then the polarizability derivative will be near zero, and the intensity of the Raman band will be low. The vibrations of a highly polar moiety, such as the O-H bond, are usually weak.

An external electric field cannot induce a large change in the dipole moment and stretching or bending the bond does not change this. Typical strong Raman scatterers are moieties with distributed electron clouds, such as carbon-carbon double bonds. The pi-electron cloud of the double bond is easily distorted in an external electric field. Bending or stretching the bond changes the distribution of electron density substantially, and causes a large change in induced dipole moment.

Chemists generally prefer a quantum-mechanical approach to Raman scattering theory, which relates scattering frequencies and intensities to vibrational and electronic energy states of the molecule. The standard perturbation theory treatment assumes that the frequency of the incident light is low compared to the frequency of the first electronic excited state. The small changes in the ground state wave function are described in terms of the sum of all possible excited vibronic states of the molecule.

Polarization Effects

Raman scatter is partially polarized, even for molecules in a gas or liquid, where the individual molecules are randomly oriented. The effect is most easily seen with an exciting source which is plane polarized. In isotropic media polarization arises because the induced electric dipole has components which vary spatially with respect to the coordinates of the molecule. Polarized Raman experiments can be a power tool in studying the mechanism of orientation and the final structure of polymeric films and fibers as well as in the characterization of single crystals.

Resonance-Enhanced Raman Scattering

If the wavelength of the exciting laser is within the electronic spectrum of a molecule, then the intensity of some Raman-active vibrations increases by a factor of 102 – 104. This resonance enhancement or resonance Raman (RR) effect may be useful. Resonance enhancement does not begin at a sharply defined wavelength. In fact, enhancement of 5X-10X is commonly observed if the exciting laser is even within a few hundred wavenumbers below the electronic transition of a molecule. This pre-resonance enhancement may also be experimentally useful.

RR, however, is only observed in molecules possessing vibrations that can be resonantly enhanced and as such this approach is limited to certain chemistries. This limits the generalized applicability of RR for analytical applications. An in-depth review of resonance enhancement is beyond the scope of this tutorial and the interested reader is referred to specific publications on the theory and application of RR.

Surface-Enhanced Raman Scattering

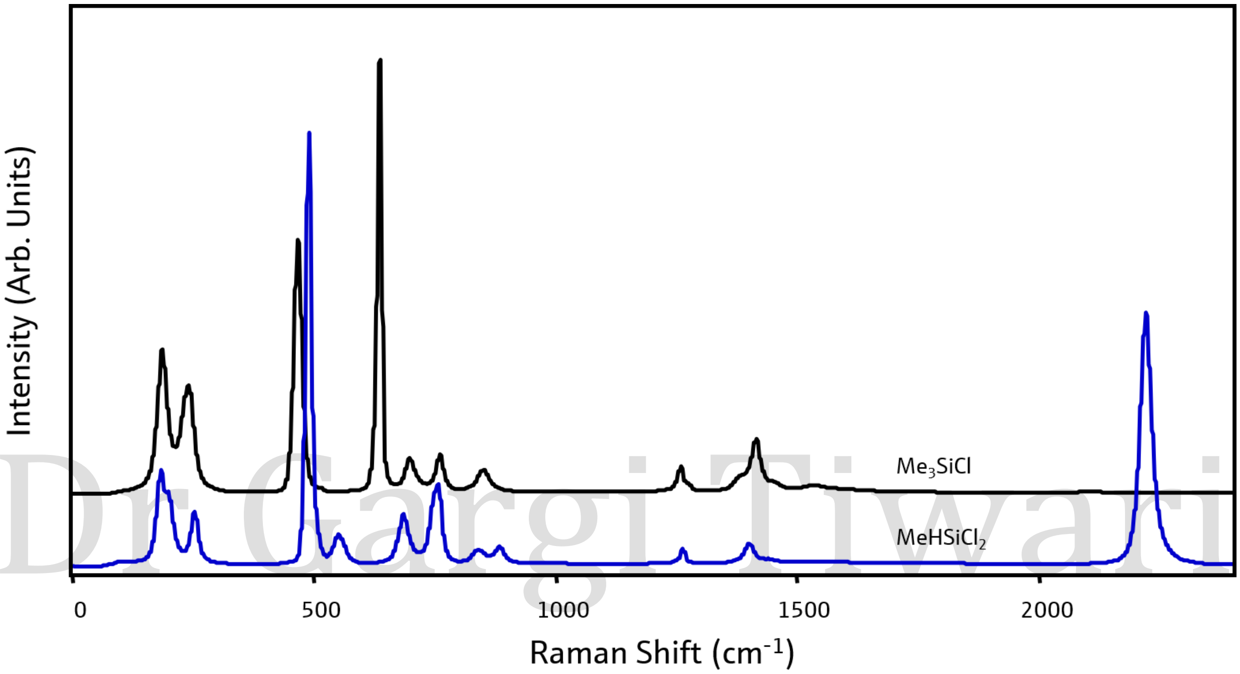
The Raman scattering from a compound (or ion) absorbed on or even within a few Angstroms of a structured metal surface can be 103 – 106x greater than in solution. This surface-enhanced Raman scattering is strongest on silver, but is observable on gold and copper as well for common excitation sources. At practical excitation wavelengths, enhancement on other metals is unimportant. Surface-enhanced Raman scattering (SERS) arises from two mechanisms.

Although SERS allows observation of Raman spectra from solution concentrations in the micromolar ($1 \text{ X } 10^{-6}$) range, slow adsorption kinetics, competitive adsorption, and the fact that only certain chemistries and states exhibit enhancements, limits the general applicability of SERS outside the R&D laboratory.

The Raman Spectrum

A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of wavenumbers, cm-1). This difference is called the *Raman shift*. Note that, because it is a difference value, the Raman shift is independent of the frequency of the incident radiation.

Note that each has a characteristic set of peaks that allows it to be distinguished from the other.



Advantages of Raman Spectroscopy

Raman spectroscopy is useful for chemical analysis for several reasons:

Specificity

Because Raman detects fundamental vibrations, Raman bands have a good signal-to-noise ratio and are non-overlapping. This allows a Raman spectrum to be used for everything from “fingerprinting” of samples to constructing complex chemical models of reaction processes.

Analysis of aqueous systems

The IR spectrum of water is strong and relatively complex, making IR inadequate for analysis of aqueous solutions due to heavy interference by the water bands. However, the Raman spectrum of water is weak and unobtrusive, allowing good spectra to be acquired of species in aqueous solution.

Analysis of organic and inorganic chemistries

If a covalent chemical bond exists between chemical species, then a unique Raman signature may be produced.

Wide Concentration Range

The measured intensity of a Raman species is directly proportional to the concentration. This allows a Raman analysis to measure a species concentration from a fraction of 1% to 100% without sample dilution.

No sample preparation

Unlike most other chemical analysis techniques, Raman requires no special preparation of the sample. In fact, no contact with the sample is needed at all because Raman involves only illuminating a sample with a laser and collecting the scattered photons.

Non-destructive Analysis

Because Raman involves only illuminating a sample, often through a window, with a laser and collecting the scattered photons, this makes Raman spectroscopy non-destructive.

Compatible with Common Windows

Raman can utilize standard sampling containers and windows manufactured of glass, sapphire, transparent polymers, and diamond to measure samples in situ.

Quantitative Raman

Because Raman involves only illuminating a sample, often through a window, with a laser and collecting the scattered photons, this makes Raman spectroscopy non-destructive.

Short measurement times

A Raman spectrum can, typically, be acquired on a timescale from a fraction of a seconds to several minutes, thus Raman can be used to monitor chemical reactions in “real time.”

In practice, because the Raman Effect is weak, the efficiency of and optimization of each of the instrumental components into an integrated system is critically important. Only an optimized system can be capable of producing the greatest measurement potential, over the widest range of same types, and able to measure the lowest concentration of species in the shortest amount of time possible.