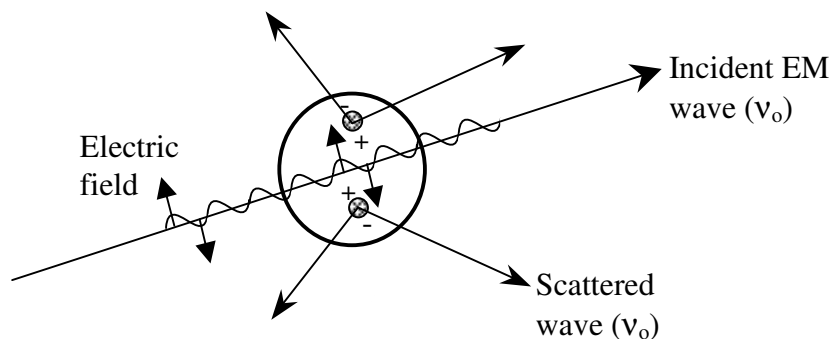# Raman Scattering Theory

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Introduction

The scattering of light may be thought of as the redirection of light that takes place when an electromagnetic (EM) wave (i.e. an incident light ray) encounters an obstacle or non-homogeneity, in our case the scattering material (solid, liquid or gas). As the EM wave interacts with the matter, the electron orbits within the constituent molecules are perturbed periodically with the same frequency (ν_o) as the electric field of the incident wave. The oscillation or perturbation of the electron cloud results in a periodic separation of charge within the molecules, which is called an induced dipole moment. The oscillating induced dipole moment is manifest as a source of EM radiation, thereby resulting in scattered light. The majority of light scattered is emitted at the identical frequency (ν_o) of the incident light, a process referred to as elastic scattering. However, as explained below, additional light is scattered at different frequencies, a process referred to as inelastic scattering. Raman scattering is one such example of inelastic scattering. In summary, the above comments describe the process of light scattering as a complex interaction between the incident EM wave and the material's molecular/atomic structure.

Figure 1. Light scattering by an induced dipole moment due to an incident EM wave.

Theory

As discussed above, an incident electromagnetic wave induces a dipole moment during the light-material interaction. The strength of the induced dipole moment, P, is given by

$$P = \alpha \overline{E}, \tag{1}$$

where α is the polarizability and $\overline{E}$ is the strength of electric field of the incident EM wave. The polarizability is a material property that depends on the molecular structure and nature of the bonds. For the incident EM wave, the electric field may be expressed as

$$\overline{E} = E_o \cos(2\pi\nu_o t), \tag{2}$$

where ν_o is the frequency (Hz) of the incident EM ($\nu_o = c/\lambda$). Substituting Eqt. (2) into (1) yields the time-dependent induced dipole moment,

$$P = \alpha E_o \cos(2\pi\nu_o t). \tag{3}$$

Because the ability to perturb the local electron cloud of a molecular structure depends on the relative location of the individual atoms, it follows that the polarizability is a function of the instantaneous position of constituent atoms. For any molecular bond, the individual atoms are confined to specific vibrational modes, in which the vibrational energy levels are quantized in a manner similar to electronic energies. The vibrational energy of a particular mode is given by

$$E_{vib} = (j + \tfrac{1}{2}) h\nu_{vib}, \tag{4}$$

where j is the vibrational quantum number (j = 0,1,2…), ν_{vib} is the frequency of the vibrational mode, and h is the Planck constant. The physical displacement dQ of the atoms about their equilibrium position due to the particular vibrational mode may be expressed as

$$dQ = Q_o \cos(2\pi\nu_{vib} t), \tag{5}$$

where Q_o is the maximum displacement about the equilibrium position. For a typical diatomic

molecule (e.g. N_2), the maximum displacement is about 10% of the bond length. For such small

displacements, the polarizability may be approximated by a Taylor series expansion, namely,

$$\alpha = \alpha_o + \frac{\partial \alpha}{\partial Q} dQ, \tag{6}$$

where α_o is the polarizability of the molecular mode at equilibrium position. Based on the

vibrational displacement of Eqt. (5), the polarizability may be given as

$$\alpha = \alpha_o + \frac{\partial \alpha}{\partial Q} Q_o \cos(2\pi v_{vib} t). \tag{7}$$

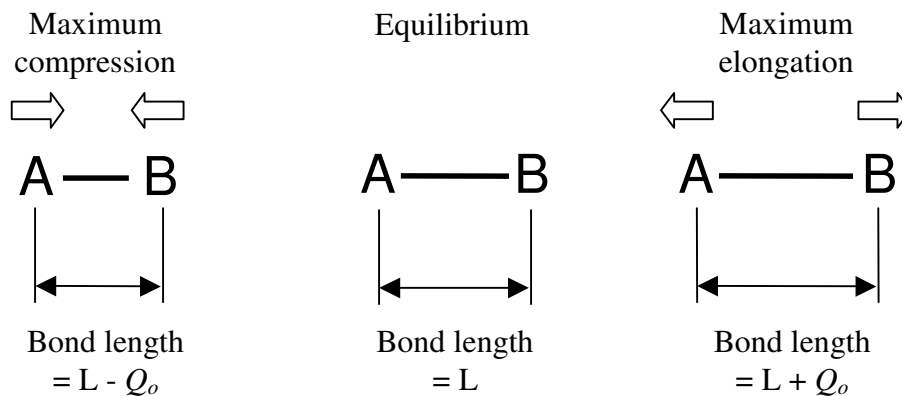Finally, Eqt. (7) may be substituted into Eqt. (3), which yields

$$P = \alpha_o E_o \cos(2\pi v_o t) + \frac{\partial \alpha}{\partial Q} Q_o E_o \cos(2\pi v_o t)\cos(2\pi v_{vib} t). \tag{8}$$

Using a trigonometric identity, the above relation may be recast as

$$P = \alpha_o E_o \cos(2\pi v_o t) + \left(\frac{\partial \alpha}{\partial Q} \frac{Q_o E_o}{2} \right) \{ \cos[2\pi(v_o - v_{vib})t] + \cos[2\pi(v_o + v_{vib})t] \}. \tag{9}$$

Examination of the above equation reveals that induced dipole moments are created at three

distinct frequencies, namely v_o, (v_o - v_{vib}), and (v_o + v_{vib}), which results in scattered radiation at

these same three frequencies. The first scattered frequency corresponds to the incident

frequency, hence is elastic scattering (e.g. Mie or Rayleigh), while the latter two frequencies are

shifted to lower or higher frequencies and are therefore inelastic processes. The scattered light in

these latter two cases is referred to as Raman scattering, with the down-shifted frequency (longer

wavelength) referred to as Stokes scattering, and the up-shifted frequency (shorter wavelength)

referred to as anti-Stokes scattering. C.V. Raman was the first to describe this type of inelastic

scattering, for which he was awarded the Noble prize in physics in 1930. Note, however, that the

necessary condition for Raman scattering is that the term $\partial\alpha/\partial Q$ must be non-zero. This condition may be physically interpreted to mean that the vibrational displacement of atoms corresponding to a particular vibrational mode results in a *change* in the polarizability. For example, consider a diatomic molecule A-B, with maximum vibrational displacement Q_o, as shown below.

Maximum compression	Equilibrium	Maximum elongation
⇨ ⇦		⇦ ⇨
A—B	A——B	A———B
Bond length = L - Q_o	Bond length = L	Bond length = L + Q_o

**Figure 2. Vibrational displacement of A-B about the equilibrium position.**

In consideration of the above figure, it is apparent that the ability to perturb the electron cloud by an incident electric field will depend on the relative position of the atoms. For example, when A-B is at maximum compression, the electrons from a given atom feel the effects of the other atom's nucleus and are therefore not perturbed as much. Hence the polarizability is reduced for the minimum bond length. In contrast, when A-B is at maximum expansion, the electrons are more readily displaced by an electric field due to the greater separation (i.e. less influence) from the other atom. Therefore, the polarizability is increased at the maximum bond length. One might make a plot of the polarizability as a function of displacement about equilibrium, which would look something like the following for the diatomic molecule A-B.

α_o

$-Q_o$ 0 $+Q_o$
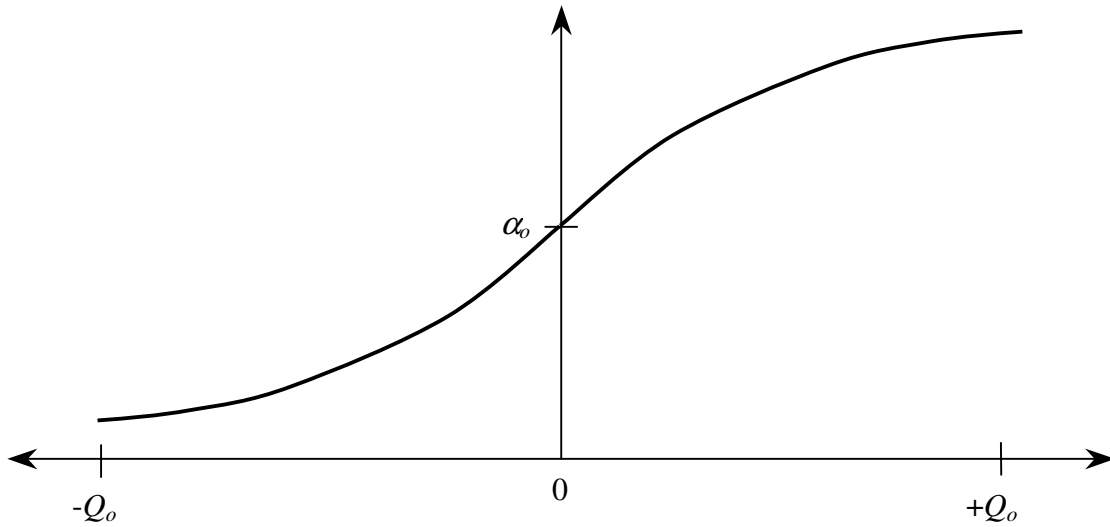
Fig. 3. Polarizability of A-B as a function of vibrational displacement about equilibrium.

It is apparent from Fig. 3 that the value of $\frac{\partial \alpha}{\partial Q}$ about the equilibrium position (at $dQ = 0$) is

non-zero; hence the fundamental vibrational mode of the diatomic molecule A-B would be

Raman active and would generate inelastically scattered light at the two frequencies $(\nu_o - \nu_{vib})$

and $(\nu_o + \nu_{vib})$. The necessary condition that the polarizability must change with vibrational

displacement (i.e. non-zero $\frac{\partial \alpha}{\partial Q}$ about equilibrium) may be thought of as the Raman selection

rule.

The above comments provide a classical framework for the understanding of Raman

scattering. However, it is also useful to describe Raman scattering in terms of the discrete

vibrational energy states of each molecular vibrational mode. This is commonly done by

considering a vibrational energy well, as shown in Figure 4, where the discrete vibrational states

each correspond to the vibrational quantum numbers as described in Equation 4. Adjacent

energy levels differ by one quantum number, hence ΔE_{vib} is equal to $h\nu_{vib}$.
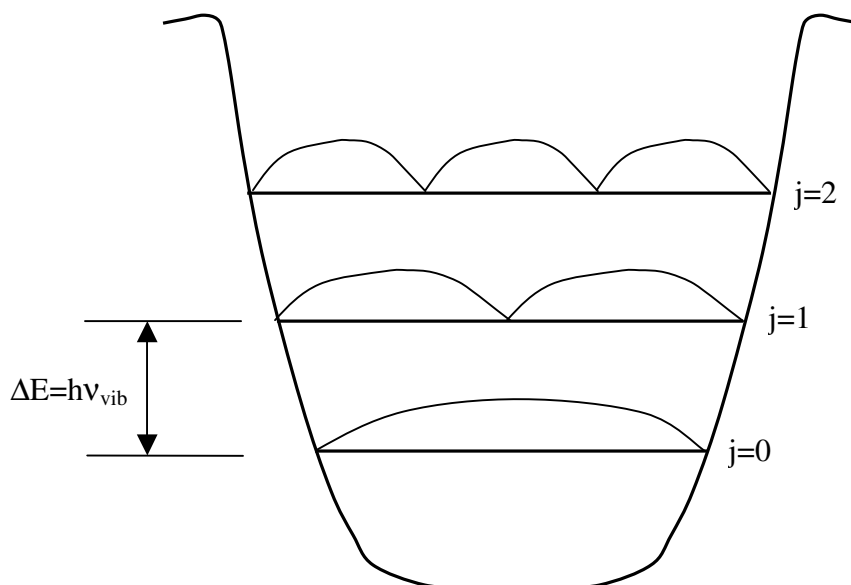
Figure 4. Vibrational energy well.

For a population of molecules, a given fraction will exist in each vibrational state, as dictated by

the Boltzmann distribution function, with the ground vibrational state (j=0) heavily favored at

low to moderate temperatures. It is noted that molecules in upper vibrational quantum states

(e.g. j=1) still vibrate at the fundamental frequency ν_{vib}, although the probability of finding the

atoms displaced about their equilibrium position changes. As an example, the curves included in

Figure 4 for each vibrational quantum level may be interpreted as the probability function of the

instantaneous displacement (*dQ*). Raman scattering may also be interpreted as a shift in

vibrational energy state due to the interaction of an incident photon. The incident EM wave

induces an oscillating dipole moment, as discussed above, thereby putting the molecular system

into a virtual energy state. The energy level of the virtual state is generally much greater than the

vibrational quanta, but is not necessarily (and generally not) equal to any particular electronic

quantum energy. Therefore, the molecule stays in its ground electronic state. However, during

the interaction with the incident photon (considering the energy of the EM wave), some quantum

of energy equal to the vibrational mode may be imparted to the molecule, as shown in Figure 5.

As a result, the remaining quantity of photon energy (which is now less than the incident photon)

leaves the molecule as Raman scattered (i.e. inelastically scattered) radiation.
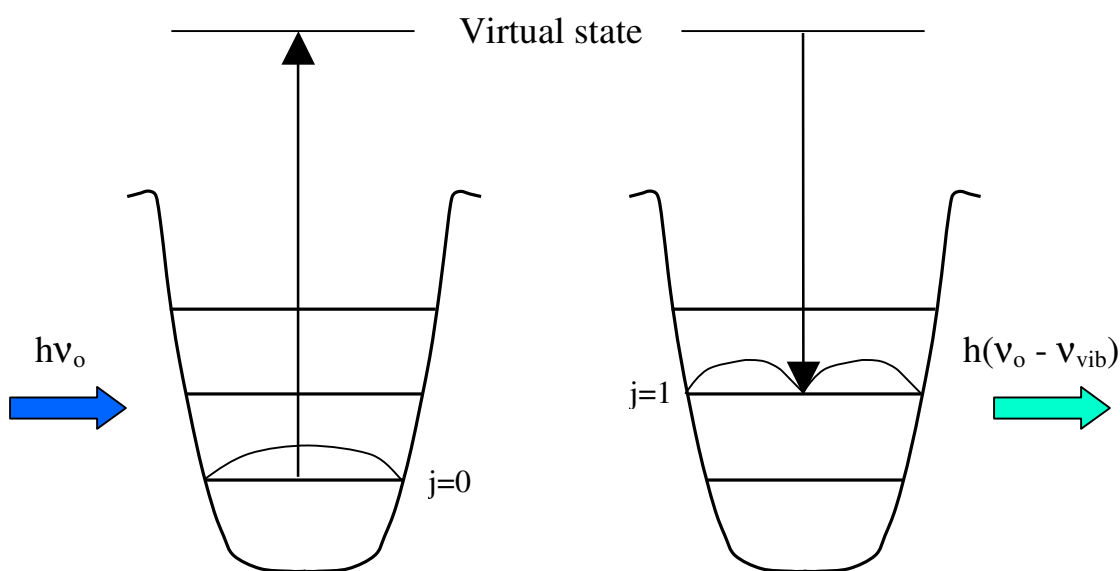
Figure 5. Conservation of energy for Raman scattering (Stokes shift).

Because the molecular system is much more likely to be originally found in the ground

vibrational state, the Stokes scattering as depicted above is the most common Raman scattering

process. For the case of Anti-Stokes scattering, the molecule is originally found in an excited

vibrational state (e.g. $j=1$). During the interaction of the incident photon with the molecule, the

vibrational energy state is relaxed back to a lower level ($\Delta j = 1$), and the vibrational quantum of

energy associated with the change in vibrational state is then added to the incident photon,

resulting in a scattered photon of energy $h(\nu_o + \nu_{vib})$. For a large system of molecules, it is

expected that both Stokes and anti-Stokes Raman scattering will occur simultaneously, with the Stokes scattering intensity generally greatly exceeding the anti-Stokes scattering intensity.

Raman Spectroscopy

In practice, Raman spectroscopy is generally performed with a laser as the excitation source because this intense, collimated monochromatic light source enables measurement of relatively small Raman shifts, while the intense beam allows for improved spatial resolution and signal-to-noise ratio. In general, the Raman signal intensity is orders of magnitude weaker than the elastic scattering intensity, hence stray light can be a considerable issue. For example, diatomic nitrogen (N_2) has an elastic scattering cross-section (i.e. Rayleigh scattering) of 8.9×10^{-28} cm^2/sr, and a Raman scattering cross-section of 5.5×10^{-31} cm^2/sr, at the wavelength 488 nm. Therefore, the Raman scattering signal is more than 1000 times weaker than the Rayleigh signal. For solids, this difference can by more than 10^6. While spectrometers are generally used to separate the elastic scattering and Raman scattering signals, the large mismatch in scattering intensity can enable the elastically scattered light to dominate the Raman light via stray light. Therefore, notch filters or edge filters (sharp cut-off high pass filters) are used to reject the elastically scattered light prior to entering the spectrometer.

Selection of the excitation wavelength (i.e. laser wavelength) depends on several factors. The Raman differential scattering cross-section (cm^2/sr) varies inversely with the fourth power of the excitation wavelength by the proportionality formula:

$$\sigma' \propto \left(\tilde{\nu}_o - \tilde{\nu}_{vib} \right)^4, \tag{10}$$

where $\tilde{\nu}_o$ is the wavenumber of the incident radiation ($1/\lambda_o$) and $\tilde{\nu}_{vib}$ is the wavenumber of the vibrational mode (ν_{vib}/c). The common unit for wavenumber (which is considered a unit of energy) is the cm^{-1}, and $\tilde{\nu}_{vib}$ generally ranges from about 200 to 4000 cm^{-1}. For example, the N_2

discussed above has a fundamental vibrational mode corresponding to $\tilde{\nu}_{vib}$ = 2331 cm^{-1}. The cross-section of 5.5x10^{-31} cm^2/sr at 488 nm would be reduced to 1.7x10^{-31} cm^2/sr at 632 nm, a reduction of more than a factor of 3. Therefore, selecting a shorter laser wavelength can increase the Raman scattering cross-section. However, as laser energies reach into the shorter visible and UV wavelength range, fluorescence (a different inelastic scattering process in which incident photons are absorbed, undergo internal conversion, and are subsequently re-emitted at longer wavelengths) can become pronounced, which may interfere with weaker Raman signals. In addition, the Raman shift is constant with regard to vibrational energy, hence constant in wavenumber, but not wavelength. Consider again the N_2 vibrational mode of $\tilde{\nu}_{vib}$ = 2331 cm^{-1}. An incident wavelength of 355 nm would be shifted to a wavelength of 387 nm, for a difference of 32 nm. Alternatively, an incident wavelength of 632 nm would be shifted to a wavelength of 741.2 nm, for a difference of 109.2 nm. A greater Raman shift makes separating the elastically scattered and Raman scattered light much easier, possibly resulting in improved signal-to-noise ratios and the ability to measure smaller Raman shifts. In summary, the Raman excitation wavelength should be selected in consideration of the Raman scattering cross-section, the magnitude of the Raman shift in wavelength, and the potential for fluorescence.

Reference

Although there are a number of books that cover the topic of Raman scattering, I don't consider any particular book to be *the* classic treatment. I have found the following texts useful for studying Raman scattering.

N.B. Colthup, L.H. Daly, S.E. Wiberley. *Introduction to Infrared and Raman Spectroscopy*. (Third Edition) Academic Press, 1990.

Derek A. Long. *The Raman Effect*. John Wiley & Sons, New York, 2002.

A. Weber (Editor). *Raman Spectroscopy of Gases and Liquids*. Topics in Current Physics. John Springer-Verlag, Berlin, 1979.

Raman Scattering Data

The following plots provide a few examples of Raman scattering behavior for gaseous, liquid, and solid samples.
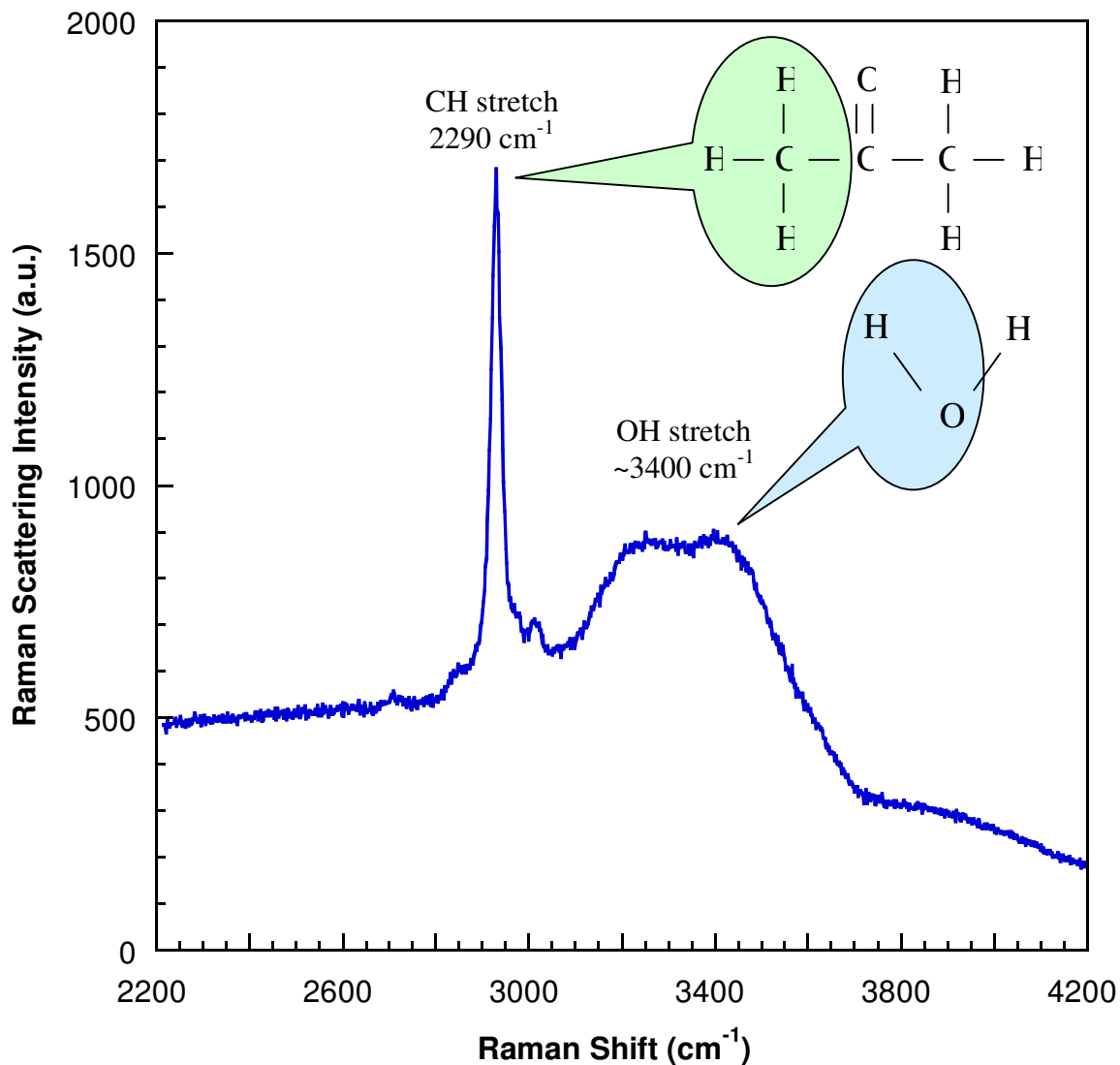
Figure 6. Raman spectrum of a liquid solution of 80% water and 20% acetone. The spectrum was recorded using a micro-Raman spectrometer with a 632.8-nm He:Ne laser as the excitation source. The various vibrational modes are noted in the figure corresponding to the water and acetone molecules, noting the uniqueness of these two stretching modes.
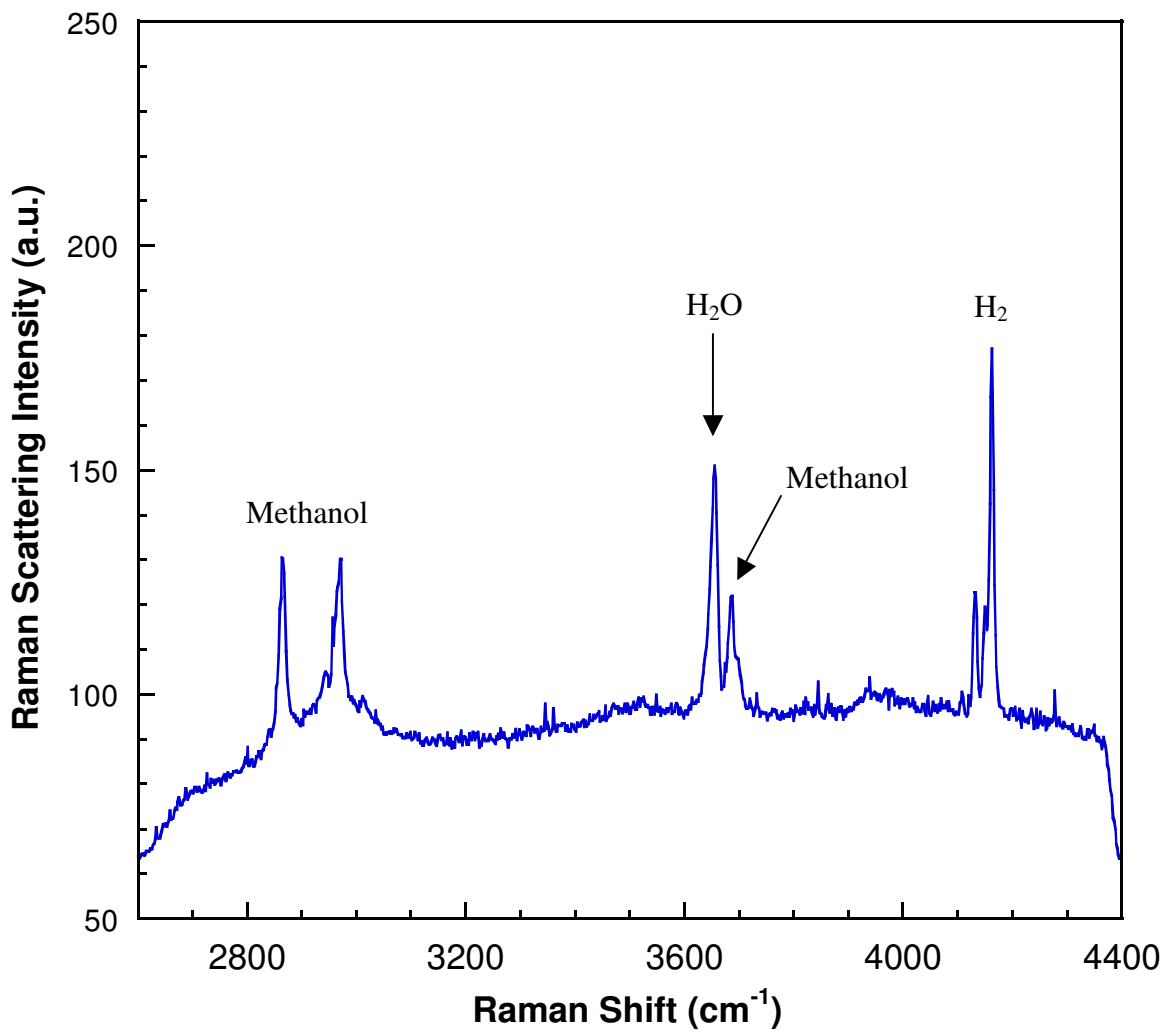
Figure 7. Raman spectrum of gas phase species recorded during reformation of methanol in a catalytic reactor. Spectrum was measured using a 355-nm pulsed laser as the excitation source, and recorded using a 0.275-m spectrometer and ICCD detector. A sharp edge filter was used prior to the spectrometer entrance. Methanol vapor Raman bands are present at 2844, 2960, and 3888 cm^{-1}, the water vapor band is present at 3654 cm^{-1}, and the hydrogen band is present at 4156 cm^{-1}.
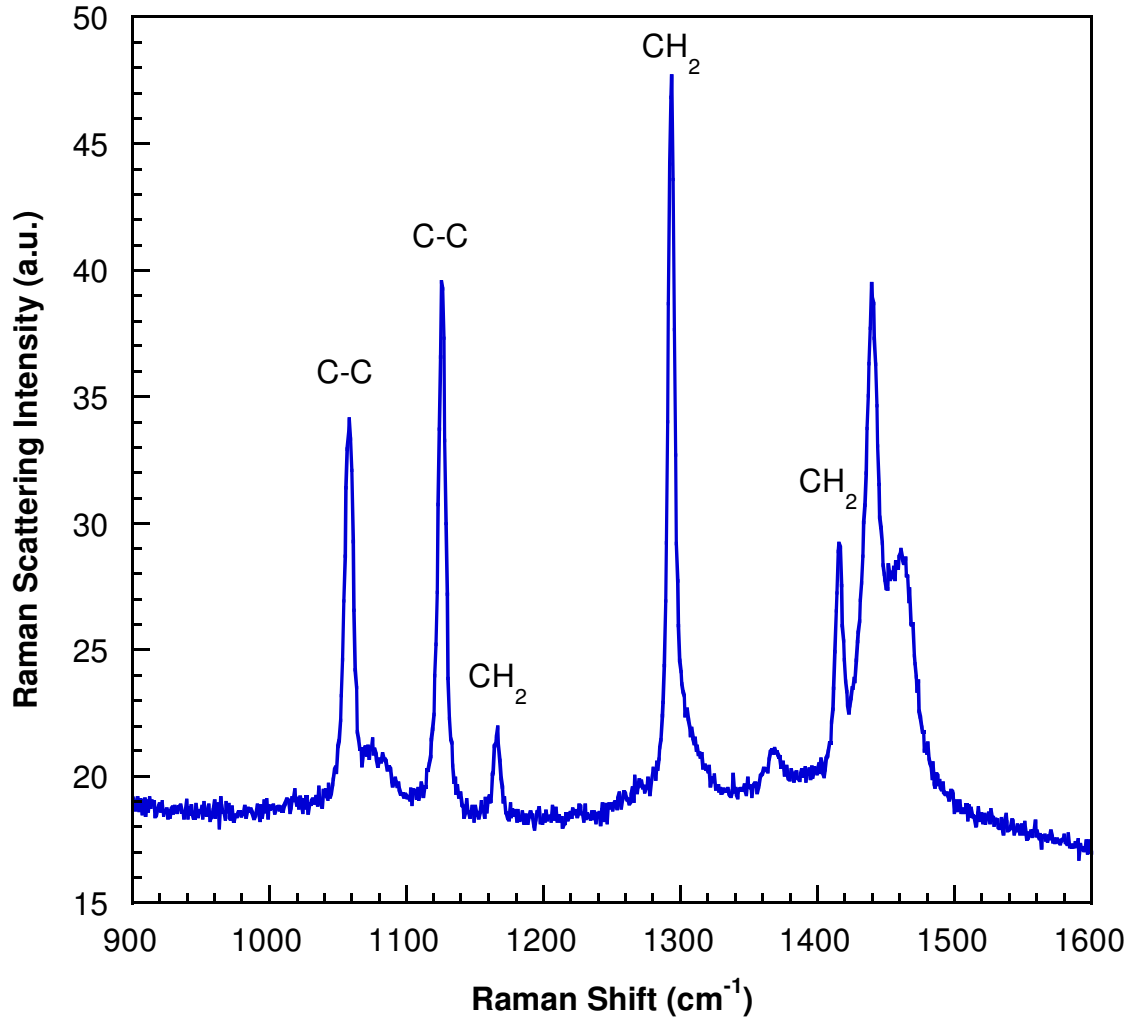
Figure 8. Raman spectrum of bulk ultrahigh molecular weight polyethylene (UHMWPE). The spectrum was recorded using a micro-Raman spectrometer with a 632.8-nm He:Ne laser as the excitation source. The various vibrational modes are noted in the figure.