

GROUP VIB' FREQ'S

FORCE CONSTANT INCREASES ↓

SMALLER MASS {

BOND	ν (cm ⁻¹)
C-C, C-O, C-N	800-1300
C=C, C=O, C=N, N=O	1500-1900
C≡C, C≡N	2000-2300
C-H, O-H, N-H	2700-3800

(USE TO STUDY H-BONDING)

H-BOND WEAKENS R-O-H 
OH BOND, LOWERS VIB' FREQ

$$\omega_0 = 2\pi\nu_0 = \sqrt{\frac{k}{\mu}}, \mu = \frac{m_1 m_2}{m_1 + m_2}$$

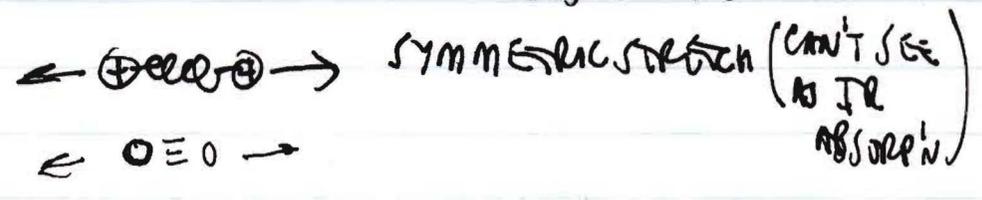
IDENTIFY VIB' BY ISOTOPIC SUBSTITUTION: ¹²C → ¹³C
OR ¹⁶O → ¹⁸O
OR ¹H → ²H

Problems: 1.66×10^{-27} kg

{	¹² C ¹⁶ O	$\bar{\nu}_0 = 2170 \text{ cm}^{-1}$	a) Calc Force constant (+ unit)
			b) Calc $\bar{\nu}_0$ for ¹³ C ¹⁶ O
	¹ H ³⁵ Cl	$\bar{\nu}_0 = 2890 \text{ cm}^{-1}$	a) Calc Force const
			b) Calc $\bar{\nu}_0$ for ² H ³⁵ Cl

Monitor Applications: Polymer formation, Identify func'l groups, much more sensitive than NMR, H-bonding (esp. DMSO), fingerprint (automobile taillight dye)

IR SELECTION RULE: DIPOLE MOMENT CHANGES DURING VIBRATION



MAXWELL:

RAYLEIGH SCATT ^{Amplitude} $\propto e^{-\text{scat'n}}$

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SCATT'G \propto Know Amplit $\propto e^{-\text{scat'n}}$

$c^{-\text{posit'n}} \propto \cos \omega t$
 $\text{scat'n} = \frac{d^2 x}{dt^2} = -\omega^2 \cos \omega t$

$I_{\text{scat'n}} \propto \omega^4$

SCATT'G = SIMULT ω , $\omega \pm \omega_1$
 FREQ = DELAYED AFTER $\omega \pm \omega_1$

(Plane-polar) Blue sky
 Red sunset
 white clouds
 X-RAY
 IMAGING

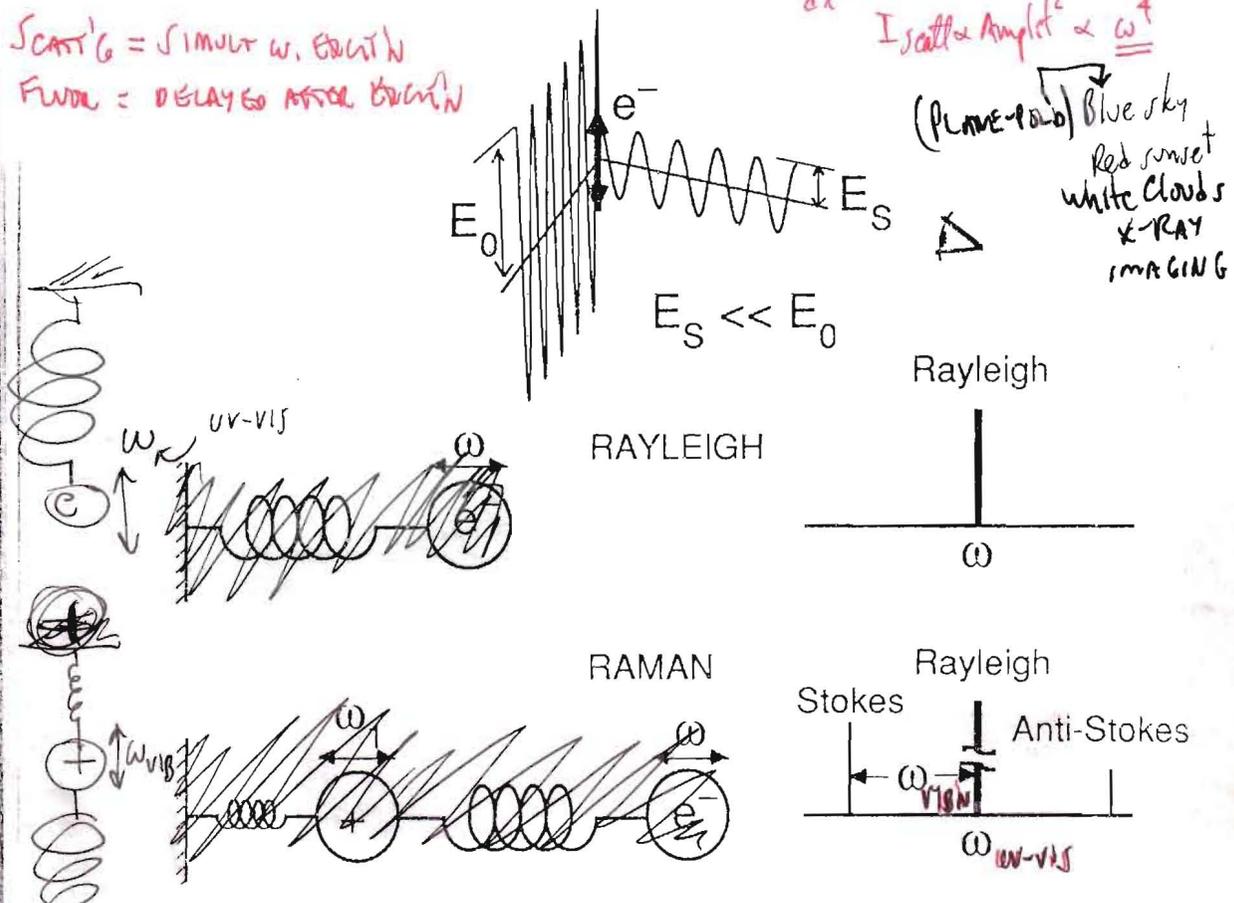


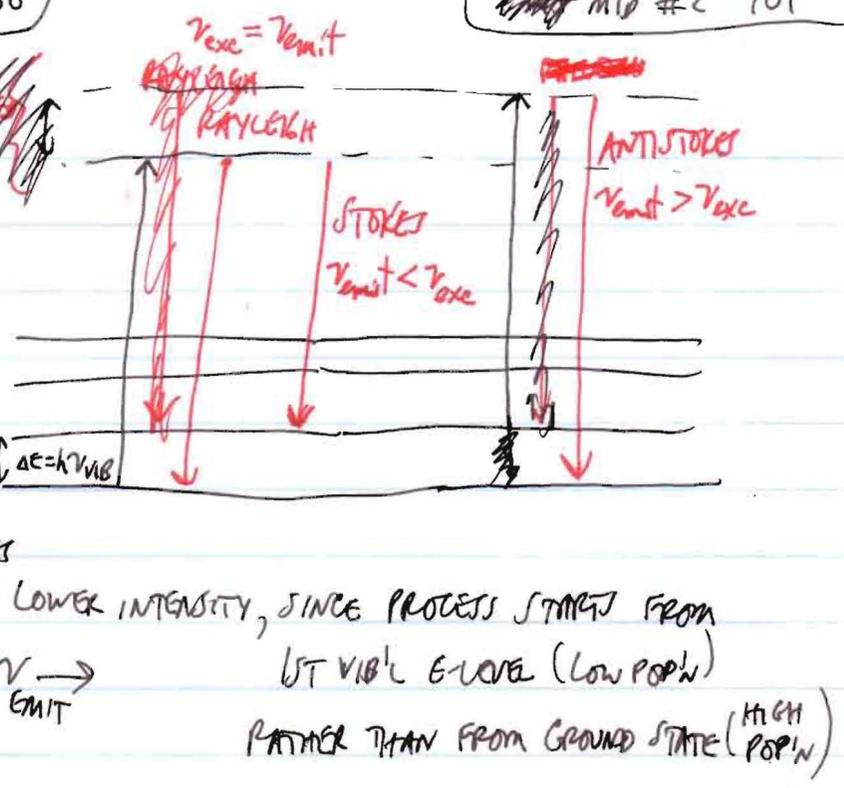
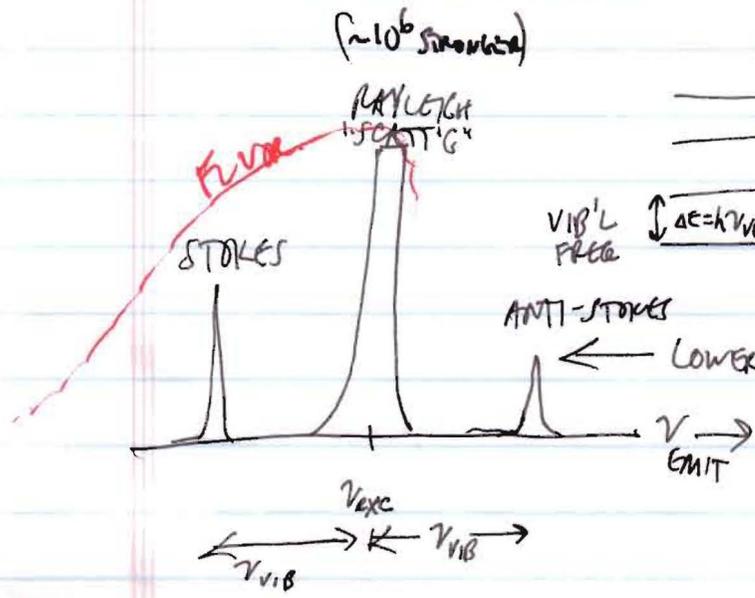
Figure 9.4 Classical description of Rayleigh (middle) and Raman (bottom) scattering. In both cases (top), an electron driven into oscillation by incident radiation, I_0 , emits radiation whose component perpendicular to the incident beam may be detected as "scattered" light, I_s . The Rayleigh component (middle) corresponds to natural vibration of the electron bound to the molecule. The (small-amplitude) vibration at frequency, ω_1 , of the atom to which the electron is bound (bottom) effectively modulates the amplitude of the electronic vibration, and therefore produces very small sidebands known as Raman scattering, located at $\omega - \omega_1$ (Stokes) and $\omega + \omega_1$ (Anti-Stokes) frequencies.

(Chapter 1.4.2) radiates (transverse) electromagnetic waves which we call "scattered" radiation. Thus, scattering may be understood by analyzing the amplitude of the electric dipole moment induced by application of an incident electric field, E .

$$E = E_0 \cos \omega t$$

(9.16)

QUANTUM MECHANICAL RAMAN



MECHANISM: AMPLITUDE MODULATION

CLASSICAL: DIPOLE MOMENT INDUCED BY ELEC FIELD OF LIGHT WAVE = $e \cdot x$

"POLARIZABILITY" \leftrightarrow $\delta^+ \delta^-$
 elec field of light $E \approx E_0 \cos \omega t$
 FREE OF LIGHT WAVE (UV-VIS)
 $e \cdot x = \alpha E = \alpha E_0 \cos \omega t$, BUT e CLOUD CHANGES SHAPE AS ATOM VIBRATE.

THEN $\alpha = \alpha_{r=r_{equilib}}$ + $\frac{d\alpha}{d(r-r_{eq})}_{r=r_{eq}}$ + ...

CHARGE \downarrow DISTANCE \downarrow

SO IF ATOM THEMSELVES ARE VIBRATING, $(r - r_{eq}) = \text{const} \cos \omega_{vib} t$

$e \cdot x = \alpha E_0 \cos \omega t$
 and $e \cdot x = \alpha_{r=r_{eq}} E_0 \cos \omega t + \text{const} \cdot E_0 \frac{d\alpha}{d(r-r_{eq})}_{r=r_{eq}} \cos \omega t \cos \omega_{vib} t$

$\cos \alpha \cos \beta = \frac{1}{2} (\cos(\alpha + \beta) + \cos(\alpha - \beta))$

AMPLITUDE MOD'N OF e MOTION BY ATOM VIB'NS

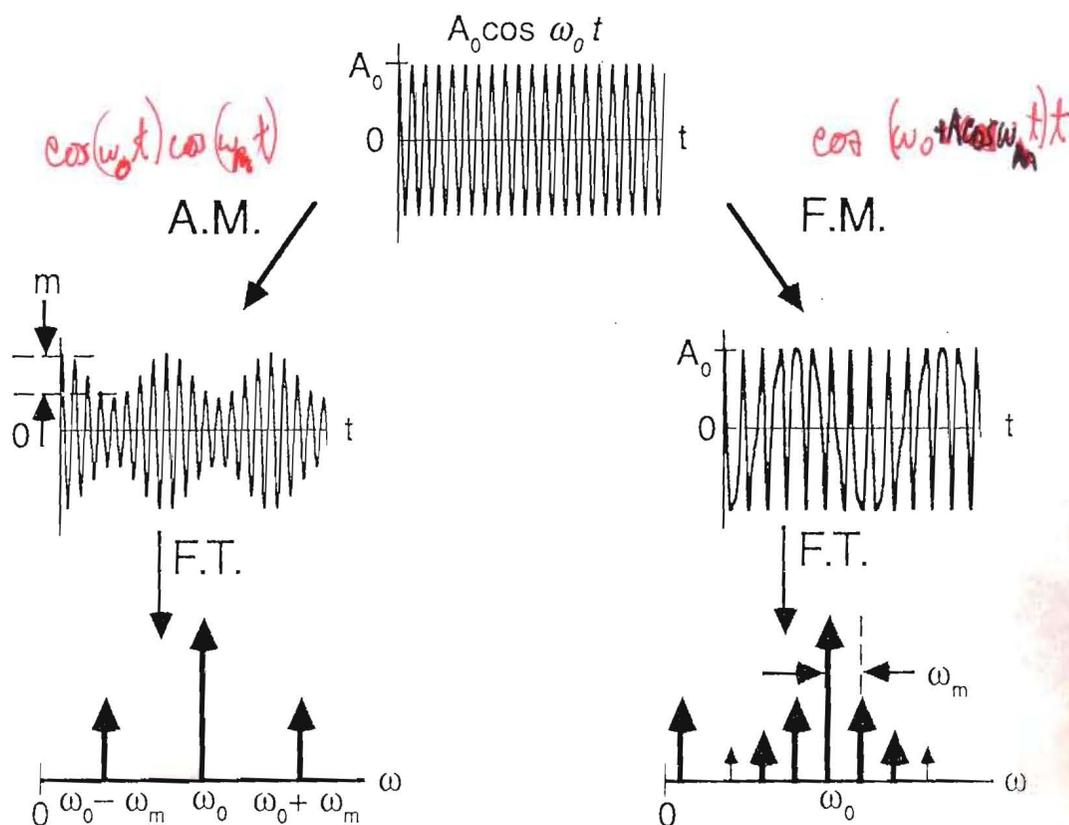


Figure 4.23 Amplitude modulation (left) and frequency modulation (right) of a sinusoidal time-domain signal (top), and corresponding frequency-domain spectra (bottom). In both cases, the spectrum shows a peak at the fundamental frequency of the unmodulated signal, as well as sideband peaks at frequencies spaced by (for AM) or at integral multiples of (for FM) the modulation frequency above and below the fundamental frequency. The relative magnitudes of the sidebands are determined by the modulation "index", m , which is defined differently for the two cases (see text).

Amplitude modulation is a common source of sidebands in spectroscopy. For example, electronic motion in a molecule can be modeled as an electron bound by a spring to a rigid molecular frame, vibrating at a natural frequency in the uv-visible frequency range. However, the nucleus to which a given electron is bound can itself vibrate at a much lower (infrared) frequency. The nuclear motion therefore modulates the amplitude of the electron displacement. In the spectrum of light radiated (scattered) by that electron, the peak at the fundamental frequency, ω_0 , is called the Rayleigh line, and the two sidebands are called the Stokes ($\omega_0 - \omega_m$) and anti-Stokes ($\omega_0 + \omega_m$) Raman peaks (see Chapter 9.1.2). As another example, NMR signals can be amplitude-modulated by sinusoidal variation in the "Q" of the receiver circuit during sample spinning.

Selection Rules

IR NEED CHANGE IN DIPOLE MOMENT DURING VIB OF THAT ^{NORMAL} MODE

RAMAN " " " POLARIZABILITY " " " " "

→ USUALLY COMPLEMENTARY (e.g. H₂O Absorbs in IR but ^{does} not ^{emit} RAMAN)

RAMAN: CAN PERFORM IN H₂O (BIOLOGICAL SAMPLES) ^{ESP.}

SOLID OR LIQ. SAMPLES BUT FLUORESCENCE

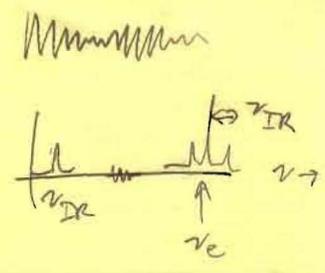
IR: PROTON VIBS, POLYMER FUEL GROUPS

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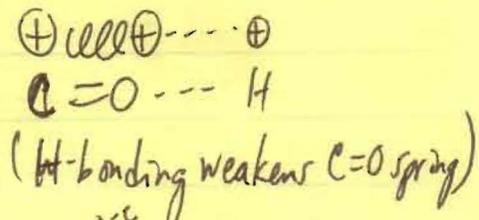
Avoid Fluor by op'g in NEAR-IR
 BUT ($I_{scatt} \propto \nu^4$)
~~But~~ so lose ~~sig~~ SIGNAL BY 10X.

IR For PROTEINS

N-H stretch	$\leftarrow N-H \rightarrow$	FREE 3300 cm^{-1}
Amide I	$\leftarrow C=O \rightarrow$	1660 cm^{-1}
Amide II	$\leftarrow C \begin{matrix} \uparrow H \\ \downarrow N \end{matrix} \rightarrow$	1550 cm^{-1}



H-bonding shifts the peaks to lower energy:



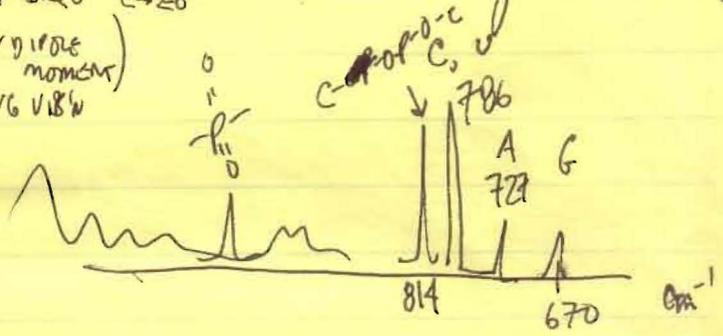
CANT SEE BY IR $\leftarrow C \rightarrow O$
 (NO CHANGE IN DIPOLE MOMENT DURING VIB)
 $\begin{matrix} O \leftarrow C \rightarrow O \\ | \\ H \end{matrix}$

Raman O-O stretch

Peroxide

O_2	1555 cm^{-1}
O_2^-	1107
H_2O_2	878
$Hb:O_2$	1107
Hemerythrin: O_2	844

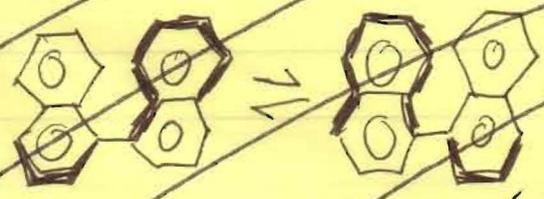
Superoxide



Why left-handed in nature?

WANT FOR C.D.

1-1 binaphthyl



Spontaneous resolu'n

% of samples

