

Lecture 10. Fundamentals of Scattering Theory 2/17/2006 ^①

* In the "Atomic Structure and Atomic Spectra", and the "Molecular Structure and Molecular Spectra", we study the "Bound States" of Particles.

The major subjects of Bound State Theory are how to derive the discrete energy eigenvalues and eigenstates, and the quantum transition probability under the interaction with external field.

In experiments, the information of Bound State is obtained by measurements of spectral lines: their wavelengths (frequencies), line intensity, line shapes, and by analyses of selection rules, etc.

* In the "Scattering Theory", we study the "Non-Bound States" of particles, which enters the continuous spectrum of energy.

What we are interested in are NOT energy eigenvalues that can vary continuously, but interested in the scattering angle distribution, scattering probability, and the change of particle properties.

In experiments, scattering angle distribution is measured at a distance far from the target ($r \gg \lambda$, where λ is the wavelength of incident particle). Thus, we want to know the wave function $\psi(r)$ when $r \rightarrow \infty$.

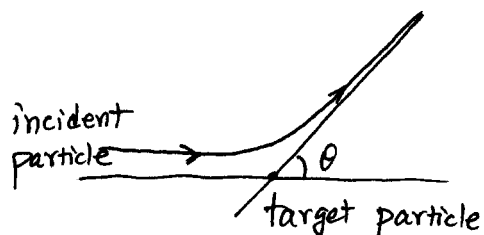
Scattering is the common approach in elementary particle physics to obtain microphysics information.

②

* A scattering process can be regarded as two-body collision.

What we want to know are

- (1) Scattering angle distribution
- (2) Scattering probability
(scattering cross-section)
- (3) changes of states or frequencies.



* QM General Theory of Scattering (2-body collision)

Hamiltonian Operator: $\hat{H} = \hat{H}_0 + \hat{V}$

Schrödinger equation: $i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H} |\psi\rangle = (\hat{H}_0 + \hat{V}) |\psi\rangle$

← Where: \hat{H}_0 is the sum of incident particle Hamiltonian operator and target particle Hamiltonian operator;
 \hat{V} is the Hamiltonian operator for interaction between the incident and target particles.

The change of state $|\psi\rangle$ from the state of free particles to the scattered state is caused by the interaction \hat{V} . If \hat{V} is regarded as a perturbation to \hat{H}_0 , we can use time-dependent perturbation theory to solve the Schrödinger equation to obtain scattering probability, etc. QM on scattering can be found at

"Landau and Lifshitz, Quantum Mechanics (Non-relativistic Theory)"

From General QM Theory of Scattering,

(3)

Elastic Scattering: only kinetic energy exchange,
no change of particle internal states

Inelastic Scattering: Kinetic energy exchange is accompanied
by change in the internal states of the colliding particles.

* We concentrate on the light scattering by particles

(atoms, molecules, and small particles)

$$\hat{H}_0 = \hat{H}_{\text{particle}} + \hat{H}_{\text{radiation}}$$

\hat{V} is the interaction between particle and radiation.

Elastic Scattering: no internal state change of particle

(i.e., ~~back~~ particle back to its initial state)

\Rightarrow no frequency change of scattered photon.

Inelastic Scattering: change of particle internal state

(i.e., particle goes to a different final state)

\Rightarrow frequency shift of scattered photon.

* In the view of Quantum Theory of Light, ④
the scattering involves the destruction (annihilation) of a photon of energy $\hbar\omega_i$ from the incident beam and the creation of a photon of energy $\hbar\omega_s$ in the scattered beam.

Thus, the light scattering is a second-order process

since two photons are involved simultaneously.

(You can't divide the annihilation of photon $\hbar\omega_i$ and the creation of photon $\hbar\omega_s$ into two separate steps. The annihilation and creation happen at the same time!)

* Spontaneous emission is a first-order process, because only one photon is involved in the process.

How about resonance fluorescence?

— ~~■~~ An atom absorbs one photon from the incident light, and then spontaneously re-emits a photon as fluorescence. Both photons are on resonance with a real transition line of the atom.

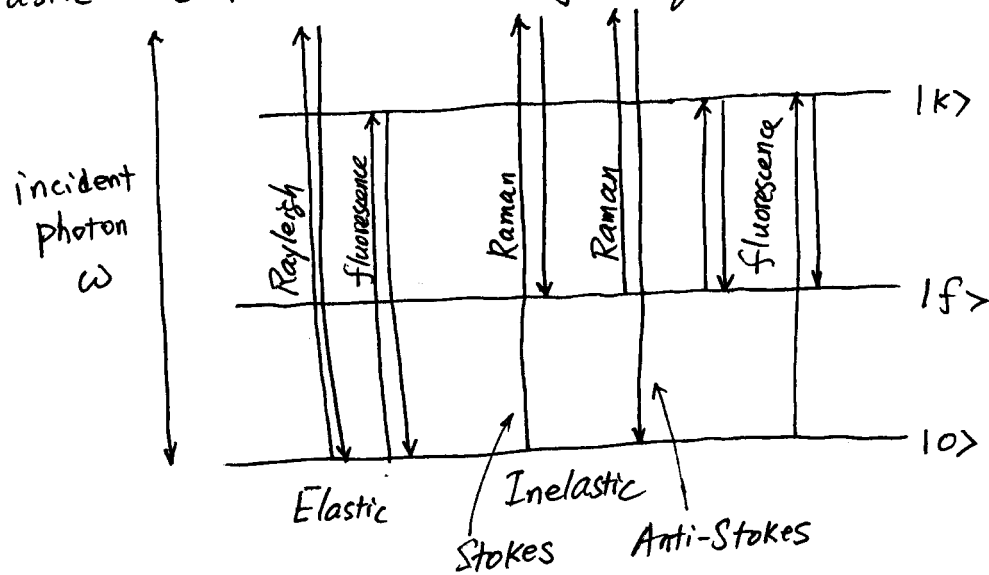
— My point of view is that resonance fluorescence is a first-order process. Although two photons are involved, they do not involve at the same time. The whole process can be divided into two separated steps: first, absorption of a photon; second, emission of another photon. The time in between

these two steps is determined by the radiative lifetime of the upper level of the transition or/and affected by the applied external radiation (if stimulated emission is resulted).

— Each step is a first-order process, thus, possessing large transition probability, i.e., effective cross-section.

For the scattering process, the second-order process results in much much smaller cross-section.

* Elastic and inelastic scattering in quantum theory of Light:



For Quantum mechanics calculation of the scattering cross-section, it is needed to have non-zero matrix element of dipole moment operator. According to Loudon "Quantum Theory of Light", the basic differential scattering cross-section for plane-polarized light radiation ω incident upon molecule:

$$\frac{d\sigma}{d\Omega} = \sum_f \frac{\omega_f \omega}{(4\pi\epsilon_0 \hbar c^2)^2} \left| \sum_k \left\{ \frac{\langle f | \hat{e}_s \cdot \hat{d} | k \rangle \langle k | \hat{e}_i \cdot \hat{d} | 0 \rangle}{\omega_{k0} - \omega} + \frac{\langle f | \hat{e}_i \cdot \hat{d} | k \rangle \langle k | \hat{e}_s \cdot \hat{d} | 0 \rangle}{\omega_{kf} + \omega} \right\} \right|^2$$

(Kramers-Heisenberg)

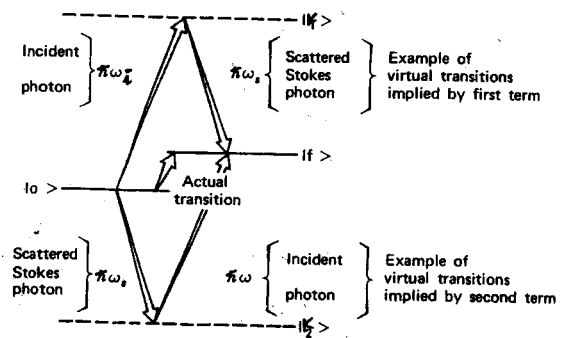
- $|0\rangle$ - initial state
- $|k\rangle$ - intermediate state
- $|f\rangle$ - final state

$$\omega_{k0} = \frac{E_k - E_0}{\hbar}, \quad \omega_{kf} = \frac{E_k - E_f}{\hbar}$$

$$\omega_f = \frac{E_f - E_0}{\hbar}$$

When $\omega_f = 0$, $|f\rangle = |0\rangle$
 \Rightarrow elastic scattering

$$\frac{d\sigma}{d\Omega} = \frac{\omega^4}{16\pi^2 \epsilon_0^2 \hbar^2 c^4} \times \left| \sum_k \left\{ \frac{\langle 0 | \hat{e}_s \cdot \hat{d} | k \rangle \langle k | \hat{e}_i \cdot \hat{d} | 0 \rangle}{\omega_{k0} - \omega} + \frac{\langle 0 | \hat{e}_i \cdot \hat{d} | k \rangle \langle k | \hat{e}_s \cdot \hat{d} | 0 \rangle}{\omega_{k0} + \omega} \right\} \right|^2$$



Actual transition from $|0\rangle \rightarrow |f\rangle$

* Physical Pictures behind the matrix

(7)

1. differential cross-section: defined as the ratio of the rate at which energy is scattered into a unit solid angle at an observation angle θ by an individual particle to the rate at which energy in the incident photon beam crosses a unit area perpendicular to its propagation direction.

$$\frac{d\sigma}{d\Omega} = \frac{w}{j}$$

w - transition/scattering rate
 j - energy flux density

2. Polarizability: is the tendency of a molecule's electrons to be deformed from its normal shape by an applied external electric field. It describes the capability of a molecule to produce induced dipole moment.

$$p = \alpha E$$

where p - induced electron dipole moment

E - external electric field

α - electronic polarizability.

3. Molecular dipole moment vs. induced dipole moment

induced dipole moment — electron

molecular dipole moment — vibration of molecule.
rotation

(1) Induced electronic dipole moment vs. elastic scattering ④

Atoms, Molecules, Small particles all have outer electrons being affected by external electric field

⇒ induced electronic dipole moment

⇒ scattering photons without freq. shift
as electrons response fast enough to radiation

⇒ Rayleigh/Carbannes scattering for Atom/molecule
($r \ll \lambda$)

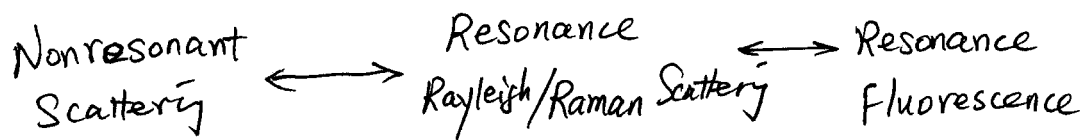
⇒ Mie scattering for small particles ($r \sim \lambda$)

(2) Molecular vibration dipole moment
vs. vibrational Raman Scattering.

(3) Molecular rotational dipole moment
vs. rotational Raman Scattering

(9)

(4) Resonance Rayleigh / Raman Scattering



Infrared and Raman Activity

Atmospheric molecules vibrate in the infrared frequencies. Depending on the mode of vibration, e. m. waves in “resonance” may change the dipole moment and/or polarizability of the molecule, leading to infrared absorption and/or Raman scattering. $p = \mu E$ or $p = \alpha E$.

Molecule	Vibration frequency	Vibration wavelength
O ₂	1555 cm ⁻¹	~ 6.4 μm
N ₂	2331 cm ⁻¹	~ 4.3 μm
CO ₂ (ν ₁ , symmetric stretch)	1388 cm ⁻¹	~ 7.5 μm
CO ₂ (ν ₂ , bending)	667.4 cm ⁻¹	~ 15 μm
CO ₂ (ν ₃ , asymmetric stretch)	2349.2 cm ⁻¹	~ 4.3 μm

The following picture demonstrate infrared and Raman activity



Symmetric stretch **Bending** **Asymmetric stretch**
 (Raman active) (Infrared active) (Raman active)

Our creator was smart to utilize symmetric diatomic molecules as majority species of our atmosphere. There is only one way to vibrate (symmetric stretch mode), which can not absorb or emit infrared emission.

Selection rules ($\Delta J = J' - J''$)

for IR absorption and Raman scattering

IR absorption: $\Delta v = \pm 1, \Delta J = \pm 1$

Raman activity: $\Delta v = 0, \pm 1; \Delta J = 0, \pm 2$

Infrared and Raman Transitions

P and R branches: $\Delta J = J' - J'' = -1, +1$

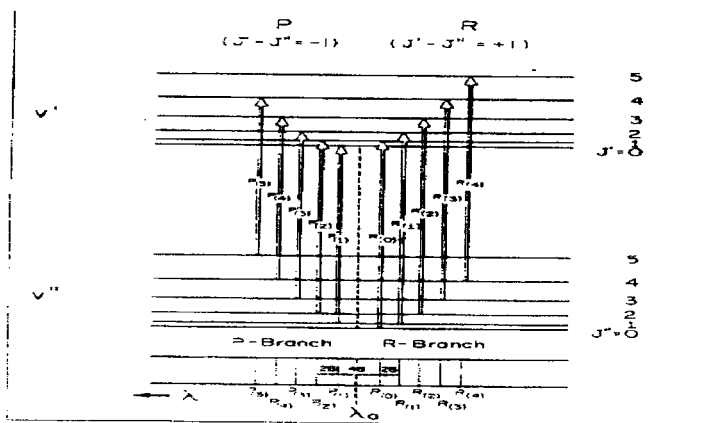
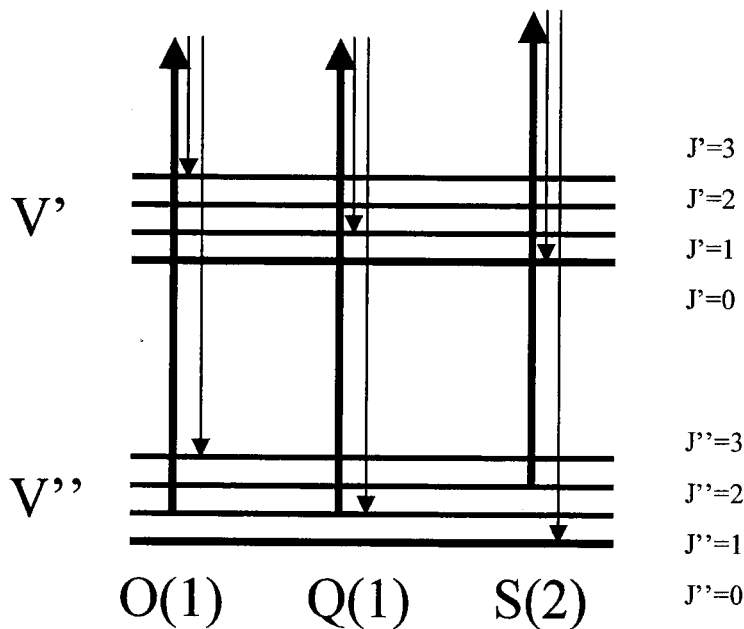


Fig. 3.9. Energy-level structure and rotational spectrum for a rigid rotator.

O, Q and S branches: $\Delta J = -2, 0, +2$



Relative Intensity in Raman Lines

Placzek and Teller factors

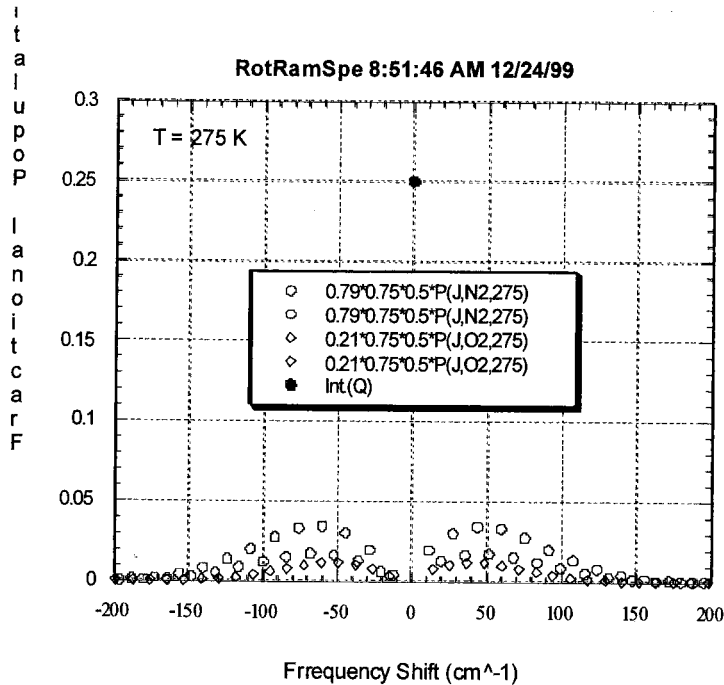
$$P_o(J \rightarrow J - 2) = \frac{3J(J - 1)}{2(2J - 1)(2J + 1)} \rightarrow \frac{3}{8} \text{ for large } J; \text{ O - Branch}$$

$$P_o(J \rightarrow J) = \frac{J(J + 1)}{(2J - 1)(2J + 3)} \rightarrow \frac{1}{4} \text{ for large } J; \text{ Q - Branch}$$

$$P_s(J \rightarrow J + 2) = \frac{3(J + 1)(J + 2)}{2(2J + 1)(2J + 3)} \rightarrow \frac{3}{8} \text{ for large } J; \text{ S - Branch}$$

Population of a vibronic state (J, v)

$$P(J, v) = (2 * I + 1) * (2 * J + 1) \exp[-E * J * (J + 1) / (0.6952 * T)] / Z(T)$$



Raman Spectra

Pure- and vibrational-rotational Raman spectra of nitrogen molecule:

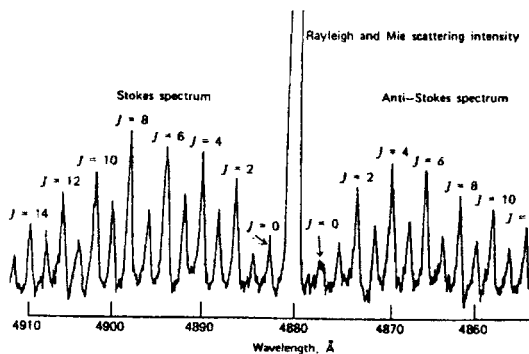
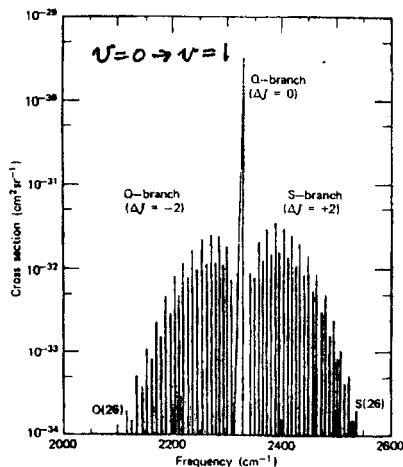


Fig. 3.24. Experimentally measured pure rotational Raman spectrum of nitrogen. Excitation wavelength 488.0 nm (Salzman, 1974).



Theoretical distribution of vibrational-rotational Raman spectrum (excitation) at 300 K, showing the O-, Q-, and S-branch structures and their cross section for N_2 molecules (Inaba and Kobayasi, 1972).

QUANTUM THEORY OF SCATTERING

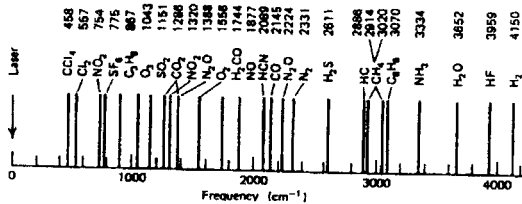


Fig. 3.23. Frequency shifts of the Q-branch of vibrational-rotational Raman spectra of typical molecular species present in polluted as well as ordinary atmosphere relative to the exciting laser frequency (Inaba and Kobayasi, 1972).

Frequency shifts of the Q-branch vibrational-rotational Raman spectra of species in a polluted air

Dipole Radiation and Rayleigh-Mie Scattering

A single particle scatters light: Mie ($a \gg \lambda$) and Rayleigh ($a \ll \lambda$).

An atom scatters light – Rayleigh scattering: induced dipole, then radiates, $p = \alpha E$.

Complication with a diatomic molecule: $\alpha = (\alpha_{\parallel} + 2\alpha_{\perp}) / 3$; $\gamma = (\alpha_{\parallel} - \alpha_{\perp})$.

Like an atom, mean molecular radius scatters light (trace scattering); in addition, random orientation also scatters light (anisotropic scattering). Since molecules rotate with characteristic frequencies, some of the anisotropic scattering is shifted in frequency. One-fourth of the anisotropic (rotational) band intensity is in un-shifted (Q-branch) and $3/4$ in the shifted part (O and S branch, often refers to as rotational Raman scattering).

Andrew T. Young, Rayleigh scattering, Physics Today, p.p. 42-48, January 1982.

Rayleigh scattering = Cabannes scattering plus rotational Raman scattering.

In the single particle regime, the Cabannes line is not resolved. It can be divided into coherent (trace scattering) and incoherent (Q-branch of RRS) parts.

The Cabannes line splits into a triplet (Gross & Brillouin) in collective regime

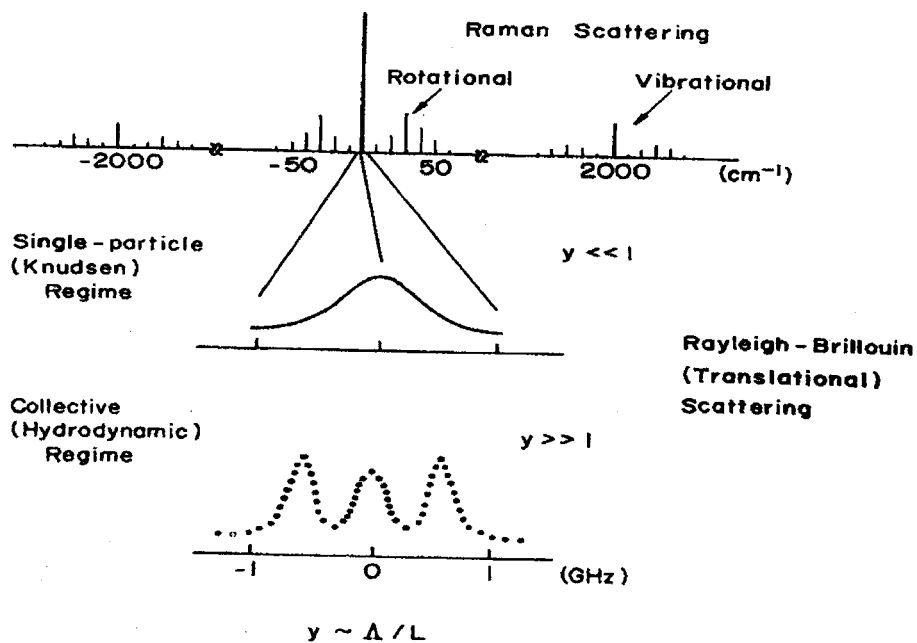


Fig. 1. Light scattering spectrum of diatomic molecules, e.g. nitrogen. The dimensionless parameter $y \sim \Delta/L$ characterizes the dynamical regime of the gas which depends on the relative values of the scattering wavelength λ and the mean-free path L

Lidars: Rayleigh, Mie, Cabannes, (pure) rotational Raman, (vib.) Raman.

Signal strength-scatter lidar

Table 3. Relative signal strength and bandwidth comparison between different scattering lidar for atmospheric parameter measurements

Bascatter Lidar	Measured Parameters (Method)	Relative Signal Strength*	Receiver Bandwidth * Night (Day)	Comments
Mie	Aerosol and cloud	> 1	5 nm (100 GHz)	Bandwidth for night (day) detection
Aerosol Wind	Wind (HET or FPI)	> 1	1 GHz, FSR	Filter bandwidth (resolution): ~ 0.1 GHz; Frequency stability: 1 ms ⁻¹ / 4 MHz
Rayleigh	Temperature (Inversion)	1	5 nm (100 GHz)	Must be aerosol free Bandwidth for night (day) detection
HSRL	Temperature (AVF; Ratio)	0.2	10 GHz	Frequency stability: 0.6 K / 2 MHz Good aerosol rejection
HSRL	Aerosol and wind (AVF; Ratio)	0.4	10 GHz	Frequency stability: 1 ms ⁻¹ / 4 MHz
Rotational Raman	Temperature (IF; Ratio)	0.005	5 nm	Filter bandwidth: ~ 1 nm; Frequency and filter stability: 10 GHz Filter OD > 6 at laser wavelength Daytime operation difficult
Vibrational Raman	Backscatter Extinction	0.001	3 nm (500 GHz)	No broader than 5 nm at night
Vibrational Raman	Temperature (Inversion)	0.001	5 nm (100 GHz)	Bandwidth for night (day) detection Problematic with extinction gradient
Molecular Wind	Wind and Temperature (Double FPI)	0.1	10 GHz, FSR	Problematic with aerosol Filter bandwidth (resolution): ~ 1 GHz Frequency stability: 1 ms ⁻¹ / 4 MHz

* See text for the definition of HET, FPI, AVF, IF and FSR

She, Chiao-Yao, Spectral structure of laser light scattering revisited: bandwidths of nonresonant scattering lidar, Appl. Opt. 40, 4875-4884, 2001.

Summary and Conclusion

The processes that are important in optical probing of atmosphere are relatively simple: one photon processes (absorption, emission and fluorescence) and two photon (scattering) processes (Rayleigh and Raman scattering). Atom and molecular structures can be understood in terms electronic transition, molecular vibrational and rotational transitions, each was 'designed' to have a different energy scale.

Depending on the mode of vibration and molecular symmetry, infrared frequency can induce vibrational transition (one photon exchange).

Visible light, however, interacts with electrons and alter their states via absorption and emission associated with an electronic transition. Non-resonant visible photon can disturb an atom or a molecule via two

photon (scattering via 'virtual' electronic transitions) processes only. In this case, molecular structure dictates the polarization property of the scattered light via isotropic and anisotropic polarizability. The basics on the structure of atoms and molecules, and on the one photon and two photon processes is explained conceptually in this lecture.

Understanding the frequency spectrum, strength and polarization property associated with various light emission, absorption and scattering processes of all atmospheric species will go a long way toward mastering remote sensing of the atmosphere. For example, such knowledge allows comparison of signal strength and of required transmitter and receiver bandwidths.

Lecture 10. Light Scattering Theory

2/17/2006

Polarizability vs. Electric Dipole

Polarizability: is the ~~relative~~ tendency of a molecule's electrons to be deformed by an ~~applied~~ ^{external} electric field.

induced dipole moment ^{from its normal shape}

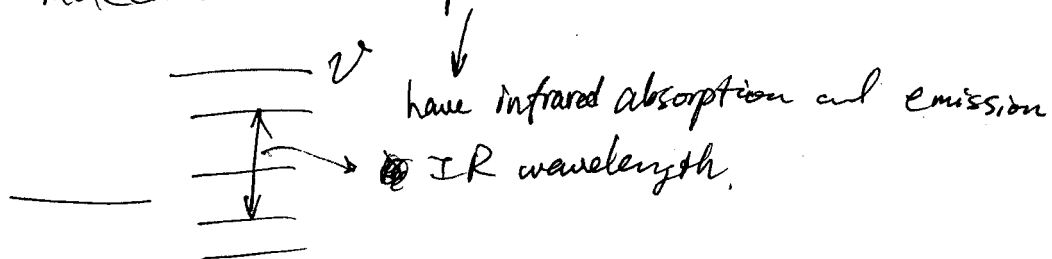
$$P = \alpha E$$

↑ ↙ ↘
electronic polarizability electric field

Induced electronic dipole moment

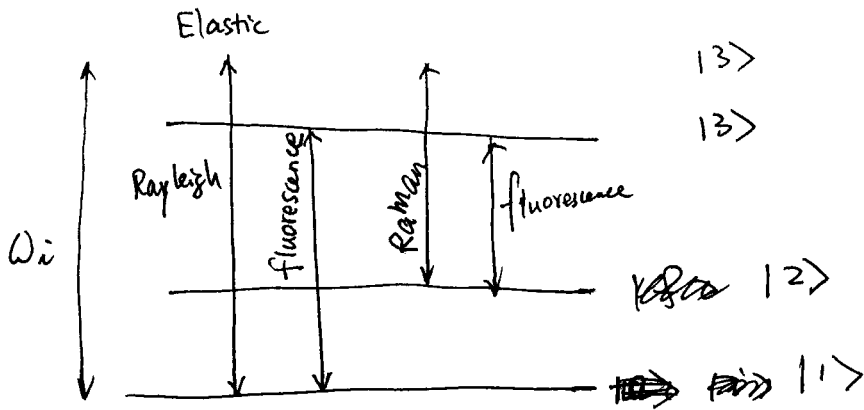
↳ Molecular dipole (intrinsic) moment.
(Vibration)

molecular vibration dipole moment caused by molecular vibration



The vibration of molecules cause change of electron polarizability \Rightarrow cause change of scattered freq.

$\omega_0 \neq \omega'$: ω' is the molecular vibration frequency \rightarrow Vibrational Raman



rotation frequency (microwave) Far IR

(3) molecular rotation motion \Rightarrow cause change of polarizability / electric-dipole-moment \Rightarrow cause change of photon \leftrightarrow rotational Raman Spectroscopy molecular rotation.

$$\omega_0 \pm \omega' \pm \omega'' \quad \text{frequency (microwave)}$$

$$\omega_0 \pm \omega''$$

Resonance Raman \rightarrow grey area