Part II. Fundamentals of Molecular Spectroscopy

Chapter 8. Introduction to Molecular Structure and Molecular Spectra

§8.1. Introduction.
Molecules have diatomic molecules and polyatomic molecules.

It is said that "A diatomic molecule is an atom with one nucleus too many!" — This is well justified in the much more complicated molecular spectroscopy, compared to atomic spectroscopy.
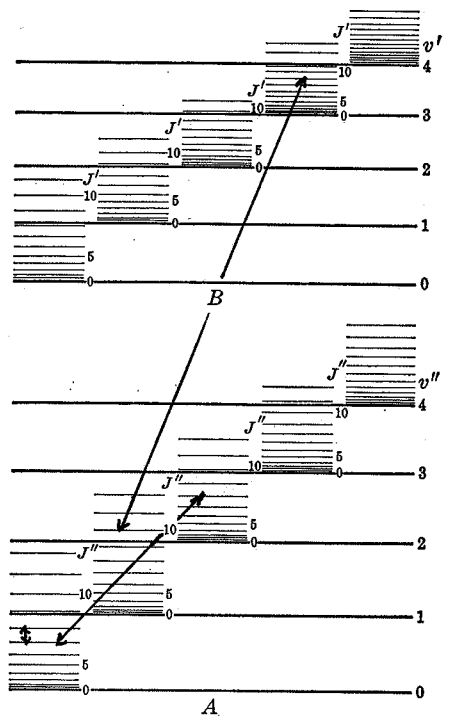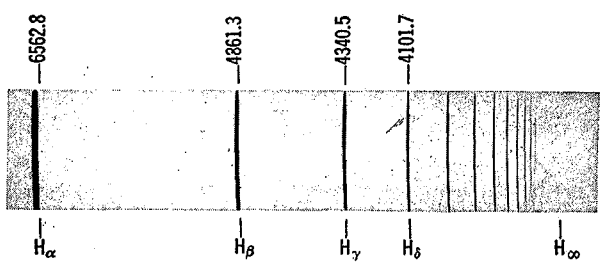


Figure 3.1. Vibrational and rotational levels of two electronic states A and B of a molecule (schematic).

The three double arrows indicate examples of transitions in the pure rotation spectrum, the rotation–vibration spectrum, and the electronic spectrum of the molecule. [from Herzberg "Molecular Spectra & Molecular Structure"]

$\left( \begin{array}{l} A \rightarrow B : \text{Visible/UV} ; \quad \upsilon \rightarrow \upsilon : \text{Infrared} \\ J \rightarrow J : \text{Microwave} \end{array} \right)$

In general, molecular energy structures have three major different energy levels : electronic energy levels (A, B), vibrational energy levels ($\upsilon''$, $\upsilon'$), and rotational energy levels ($J''$, $J'$). They are resulted from the three major motions inside a molecule : the electron motion and the nuclei motions — vibration and rotation. These complicated motions result in energy band and band spectrum of molecules, compared to atomic energy level and line spectrum.

FIG. 6. Emission Spectrum of the Hydrogen Atom in the Visible and Near Ultraviolet Region [Balmer Series, after Herzberg (302)]. $H_\infty$ gives the position of the series limit.
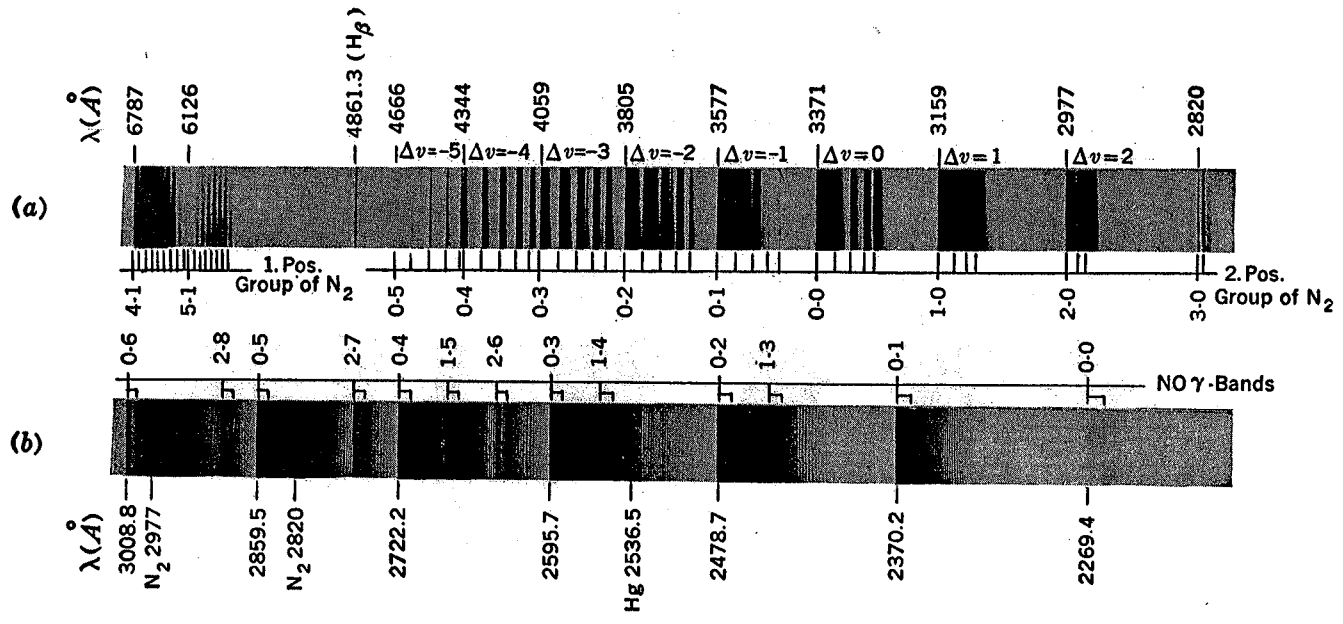
← Line Spectrum of H atom



FIG. 8. Band Spectrum of an Air-Filled Geissler Tube. (a) Long-wave-length part. (b) Short-wave-length part. The latter is much more strongly exposed than the former.

Band Spectrum of molecules

Comparison between atom and molecule :

|  | Atom | Molecules |  |
|---|---|---|---|
| Coarse Structure (Electrostatic Force) | $4 - 28\,eV$ | $1 - 20\,eV$ | Electron motion |
|  |  | $0.05 - 1\,eV$ | Nuclear Vibration |
| Fine Structure (Spin-Orbital Coupling magnetic interaction) | $10^{-4} - 10^{-1}\,eV$ | $10^{-4} - 0.05\,eV$ | Nuclear rotation |
|  |  |  | electron, nuclear Spin |
| Hyperfine Structure (Nuclear influence) | $10^{-7} - 10^{-4}\,eV$ |  |  |
|  |  |  | Translation as a whole |

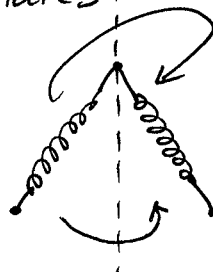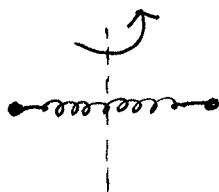Interactions / Motions with a molecule:

(1) Electron motion (mainly outer electrons) → electronic state
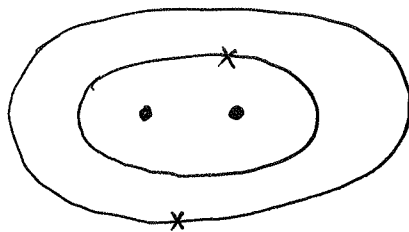


(2) Nucleus vibration → Vibrational states
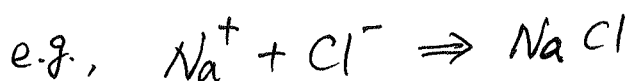


O      C      O



( $CO_2$ )
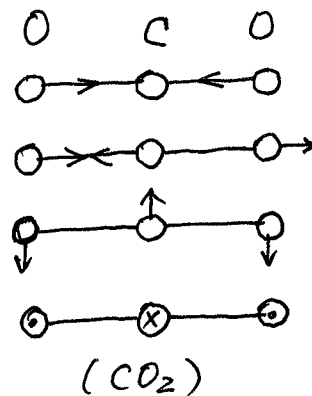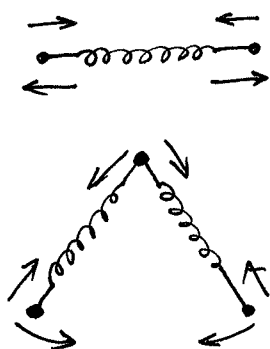
(3) Nucleus rotation → rotational states



(4) Electron spin, nuclear spin → fine and hyperfine structure of the electronic states

(5) Translation of the entire molecule → continuum energy

Chemical Bonds : electrostatic force holds atoms/molecules together

(1) Ionic Bond: electron transfer from one atom to another.

e.g., $Na^+ + Cl^- \Rightarrow NaCl$         (intramolecular force)

$\left\{\begin{array}{l} \text{Positive - negative ion} \quad \text{Coulomb attraction} \\ \text{nucleus- nucleus} \\ \text{electron - electron} \end{array}\right\}$ Coulomb repulsion $\left.\right\} \Rightarrow$ Balance

E

When two ions are apart!

$r_0$         r
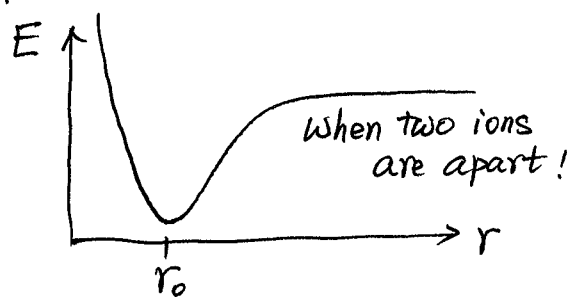
(2) Covalent Bond: valence electrons are owned/shared by both atoms

e.g., $N_2$, $O_2$, $H_2$, HCl ,         E

(intramolecular force)

r
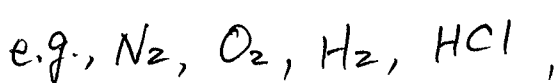
(3) Metallic Bond: "free electron gas" in metal.

e.g., Fe, Al, Na, ...

(4) Van der Waals Bond : $Hg_2$

Inter- molecular bonds

(5) Hydrogen Bond : one part of the bond involves a hydrogen atom.

inter - molecular force

## §8.2. Born – Oppenheimer Approximation (Separation)

Similar to the atomic spectroscopy, the molecular spectroscopy involves the molecular structure and molecular spectra. In principle, the methods to study them are similar to atomic spectroscopy,

i.e.,

* Molecular Structure
(determined by the interactions and motions of electrons and nuclei )
→ Energy Eigenvalue equation
( Time-Independent Schrödinger equation )

* Molecular Spectra
Radiative transition probability → Time-dependent Schrödinger equation

Spectral lineshape, etc. → Statistical information

However, molecular spectroscopy is much more complicated than atomic spectroscopy. For many cases, it is very difficult to solve the Schrödinger equations. Polyatomic molecules are even more complicated than the diatomic molecules.

* For our class, we only introduce the structure and radiative transition selection rules for diatomic molecules. The other contents are beyond our scope. You may read the classical molecular spectroscopy books, like Herzberg's "Molecular Spectra and molecular Structure", or newer books and research articles for new progresses in molecular spectroscopy study. John M. Brown's "Molecular Spectroscopy" is the right-level reference book for our class.

To derive molecular structure is, in principle, to solve the energy eigenvalue equation:

$$\hat{H} | \psi \rangle = E | \psi \rangle \qquad (1)$$

where
$$\hat{H} = \sum_i \frac{\hat{P}_i^2}{2m_e} + \sum_k \frac{\hat{P}_k^2}{2M_k} + V(\hat{\vec{r}}_i, \hat{\vec{R}}_k)$$

$$= -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k \frac{\hbar^2}{2M_k} \nabla_k^2 + V(\hat{\vec{r}}_i, \hat{\vec{R}}_k) \qquad (2)$$

( $i$ — electrons,   $k$ — nuclei )

* As the magnetic interactions within a molecule are much smaller than the electrostatic interactions, we only consider the molecule as a collection of charged, massive particles (electrons and nuclei) that move under the influence of electrostatic forces. The instantaneous position of each particle can be specified by the Cartesian coordinates, or $\hat{\vec{r}}_i$ or $\hat{\vec{R}}_k$ (for electron and nucleus).

* Even so, it is still very complicated. For our purpose, a very useful approximation based on Born-Oppenheimer separation is the approach taken in our class.

* The physical basis for the Born-Oppenheimer separation is that the electrons and nuclei are subjected to similar magnitude force (these forces are electrostatic in origin and the interaction is mutual). However, since the nuclei are about 4 orders of magnitude more massive, the electrons move much more rapidly than the nuclei. Thus, we can treat the motion of the electrons as if the nuclei were fixed in positions. Mathematically speaking, this approximation is to separate the total wave-function into an electronic and a nuclear part.

$$\psi_{total} \approx \psi_{electrons}^{(r_{el})} \psi_{nuclei}^{(r_{nucl})} \qquad (3)$$

The electronic wavefunction is a function of electronic coordinates only (for fixed internuclear separations).

In the same spirit, the nuclear motion can be further separated into a vibrational and a rotational part:

$$\psi_{total} \approx \psi_e (r_{el}) \, \psi_{vib}(r_{vib}) \, \psi_{rot}(r_{rot}) \qquad (4).$$

Under this approximation, the total energy of the molecule is a simple sum of contributions from these three types of motion:

$$E_{total} = E_{el} + E_{vib} + E_{rot} \qquad (5).$$

## §8.3. Electric Dipole Transitions versus Electric Dipole Moment

From Radiative Transition theory, we know whether a transition can occur is determined by the matrix element of the electric dipole moment [besides the resonance condition $\delta(\omega - \omega_0)$]

$$H'_{nm} \;\rightarrow\; D_{nm} = \langle \psi_n | \overset{\wedge}{\vec{D}} | \psi_m \rangle \overset{?}{\neq} 0 \qquad (6)$$

where operator $\overset{\wedge}{\vec{D}} = -e\,\overset{\wedge}{\vec{r}}.$ $\qquad\qquad (7)$

$e$ is electron charge, $\overset{\wedge}{\vec{r}}$ is the electron position vector relative to nucleus or the mass center.

So-called **permanent electric dipole moment** is defined as

$$\langle \overset{\wedge}{\vec{D}} \rangle \equiv \langle \psi_m | \overset{\wedge}{\vec{D}} | \psi_m \rangle \qquad (8)$$

i.e., the mean value of $\overset{\wedge}{\vec{D}}$ when the atom/molecule is in its energy eigenstate. That is the matrix element when $m=n$.

Due to uncertainty principle, electrons inside an atom do not have precise positions. Thus, when talking about whether an atom or a molecule has a dipole moment, we refer to the mean value of the operator $\overset{\wedge}{\vec{D}}$ under certain state conditions, i.e., take average under the conditions over certain period. It could be the permanent electric dipole moment defined in Eq.(8) or induced electric dipole moment given by Eq.(6).

(1) In case of an atom,

$$\langle \hat{\vec{D}} \rangle \equiv \langle \psi_m | \hat{\vec{D}} | \psi_m \rangle = 0, \qquad (9)$$

because $\hat{\vec{D}} = -e\hat{\vec{r}}$ and $\hat{\vec{r}}$ is antisymmetric, while all electron orbits (i.e., electron distribution of probability) are symmetric $\Rightarrow$ the mean value of $\hat{\vec{D}}$ is zero for any electron orbits.



$l=0$ (s) $\quad\langle \hat{\vec{D}} \rangle = 0$

$l=1$ (p) $\quad\langle \hat{\vec{D}} \rangle = 0$

$l=2$ (d) $\quad\langle \hat{\vec{D}} \rangle = 0$
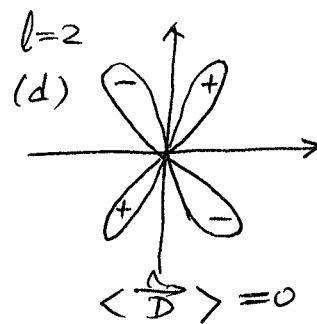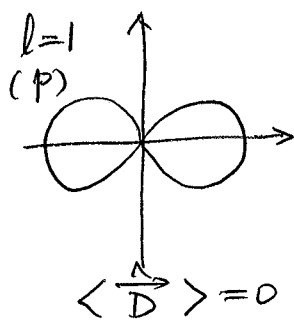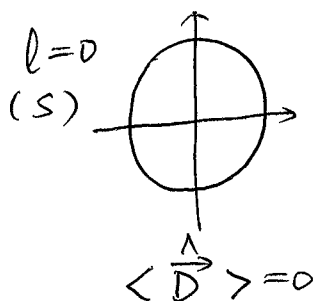
Therefore, all atoms have zero permanent electric dipole moment.

* How to understand the electric dipole transition $(E_1)$ of an atom?

In case of atoms, transition happens when electrons have state change, i.e., orbital change, e.g., from $s \to p$



$S \Rightarrow P$
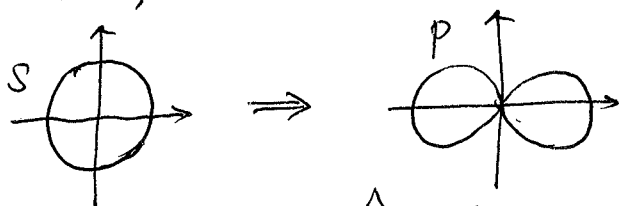
If the matrix element $\langle \psi_n | \hat{\vec{D}} | \psi_m \rangle \neq 0$, then the transition can happen. The selection rules require $\Delta l = \pm 1$.

Although $\langle \psi_i | \hat{\vec{D}} | \psi_i \rangle = \langle \psi_f | \hat{\vec{D}} | \psi_f \rangle = 0$, $\langle \psi_f | \hat{\vec{D}} | \psi_i \rangle \neq 0$.

This may be understood as the induced electric dipole moment: the radiation field (in the cases of stimulated emission and absorption) causes the center of negative charges

off the center of the positive charges (nucleus), inducing an electric dipole moment to enable the electronic transition ($E_1$ transition). In the case of spontaneous emission, although no radiation field is added, the vacuum fluctuation field can still induce an electric dipole moment, resulting in the $E_1$ transitions. — This is physical picture, classical oriented.

* Recall in the full-Quantum radiative transition theory, we introduce the vector potential → quantized $E$ and $B$ field. Then we use the momentum $\hat{\vec{P}}$ of the electrons in the Hamiltonian operator, and then utilize the commutation relationship between $\hat{\vec{r}}$ and $\hat{\vec{P}}$, we introduce $\hat{\vec{r}}$ into the picture. This $\hat{\vec{r}}$ can be understood as instantaneous position vector of the electron. However, due to uncertainty principle, the $\hat{\vec{r}}$ is not fixed, but changes all the time. The matrix element $\langle \psi_f | \hat{\vec{r}} | \psi_i \rangle$ can be understood as we take the time-mean of $\hat{\vec{r}}$ in a superposition state of $|\psi_i\rangle$ and $|\psi_f\rangle$. Since $|\psi_i\rangle$ is different from $|\psi_f\rangle$, the matrix element could be non-zero, i.e., induced electric dipole moment is non-zero. Thus, the transition can happen.

(2) In case of a molecule,

* Homonuclear diatomic molecule, e.g., $N_2$, $O_2$, $H_2$, ...

$$\langle \hat{\vec{D}} \rangle \equiv \langle \psi_m | \hat{\vec{D}} | \psi_m \rangle = 0 \qquad (10)$$

This is because the molecule is symmetry, resulting in the overlap of the negative charge center with the positive charge center. Thus, the permanent electric dipole moment is zero for homonuclear molecules.

Similar to the atomic situation, as long as $\langle \psi_n | \hat{\vec{D}} | \psi_m \rangle \neq 0$, the induced electric dipole moment still enables the homonuclear molecules to have electronic transitions between different electronic states, but no vibration and rotation spectra.

* Heteronuclear molecule, e.g., OH, CH, NO, ...

$$\langle \hat{\vec{D}} \rangle \equiv \langle \psi_m | \hat{\vec{D}} | \psi_m \rangle \neq 0 \qquad (11)$$

So the heteronuclear molecules have nonzero permanent electric dipole moment. Thus, besides the electronic transition spectra $\langle \psi_n | \hat{\vec{D}} | \psi_m \rangle \neq 0$, heteronuclear molecules can have vibration and rotation spectra,

* Let us take a further look at why homonuclear molecules won't have vibration and rotation transitions, while heteronuclear molecules will.

Homonuclear Molecule :



Electronic Transition
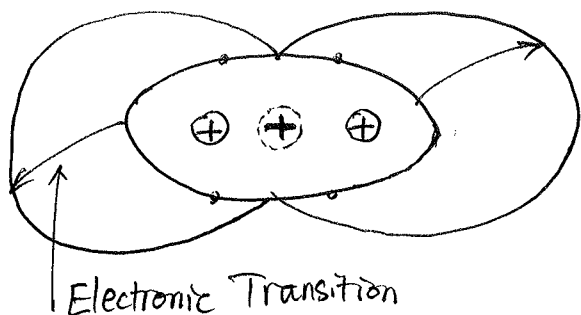
At equilibrium, the centers of positive and negative charges overlap with each other,

$$\therefore \ \langle \hat{r} \rangle = 0$$

$$\therefore \ D_0 = 0 \qquad\qquad (12)$$

The vibration and rotation of homonuclear nuclei do not change positive charge center, so it still overlaps with the negative charge center. Thus $D_1 = 0$ (13)

Where $D_1$ is the change rate of dipole moment with internuclear distance. Therefore, homonuclear molecule has

$$D = D_0 + D_1 \mathcal{X} = 0 \qquad\qquad (14)$$

Where $\mathcal{X} = r - r_e$, $r_e$ is the internuclear distance at equilibrium.

Hetero-nuclear Molecule :
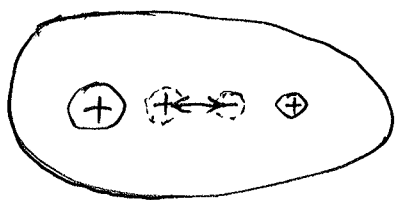


The centers of positive and negative charges do not overlap with each other.

$$\therefore \ \langle \hat{r} \rangle \neq 0$$

$$\qquad\qquad (15)$$

$$\therefore \ D_0 \neq 0.$$

$$D = D_0 + D_1 \mathcal{X} \neq 0 \qquad\qquad (16)$$

Under Born - Oppenheimer Approximation,

$$|\psi_{Total}\rangle = |\psi_e\rangle |\psi_v\rangle |\psi_R\rangle \qquad\qquad (17)$$

Thus, permanent electric dipole moment:

$$\langle \hat{\vec{D}} \rangle \equiv \langle \psi_{Total} | \hat{\vec{D}} | \psi_{Total} \rangle \qquad (18)$$

$$= \langle \psi_R | \langle \psi_v | \underbrace{\langle \psi_e | \hat{\vec{D}} | \psi_e \rangle} | \psi_v \rangle | \psi_R \rangle$$

Matrix element:

$$\langle \psi'_{Total} | \hat{\vec{D}} | \psi_{Total} \rangle$$

$$= \langle \psi_{R'} | \langle \psi_{v'} | \langle \psi_{e'} | \hat{\vec{D}} | \psi_e \rangle | \psi_v \rangle | \psi_R \rangle \qquad (19)$$

When we only consider the pure vibration − rotation transitions, $|\psi_e\rangle$ does not change, i.e., transitions within the same electronic state, $\therefore |\psi_{e'}\rangle = |\psi_e\rangle$. Then the matrix element

$$\langle \psi'_{Total} | \hat{\vec{D}} | \psi_{Total} \rangle$$

$$= \langle \psi_{R'} | \langle \psi_{v'} | \underbrace{\langle \psi_e | \hat{\vec{D}} | \psi_e \rangle} | \psi_v \rangle | \psi_R \rangle \qquad (20)$$

① If $\langle \psi_e | \hat{\vec{D}} | \psi_e \rangle = 0$ (e.g., homonuclear molecule case),
  then the above matrix element $= 0$.
  Therefore, no transitions (real transitions) in vibration and rotation spectra are allowed for homonuclear molecules.

② If $\langle \psi_e | \hat{\vec{D}} | \psi_e \rangle \neq 0$, (e.g., heteronuclear molecules),
  assume $\langle \psi_e | \hat{\vec{D}} | \psi_e \rangle = \underset{\substack{\text{(dipole moment at the} \\ \text{equilibrium position)}}}{D_0} + \underset{\substack{\text{(change rate of dipole moment} \\ \text{with internuclear distance)}}}{D_1 \hat{x}}, \quad x = r - r_e \quad (21)$

$\therefore$ Above matrix element $= \langle \psi_{R'} | \langle \psi_{v'} | D_0 + D_1 \hat{x} | \psi_v \rangle | \psi_R \rangle \neq 0$
then transitions in vibration and rotational spectra are allowed for heteronuclear molecules.

(3) In case of Scattering (Rayleigh and Raman): virtual transition
This is a two-photon process.

The incident photon $\Rightarrow$ induced electric dipole moment



$$\vec{P}_{induced} = \alpha \vec{E}$$

(no electron state change, but distortion)
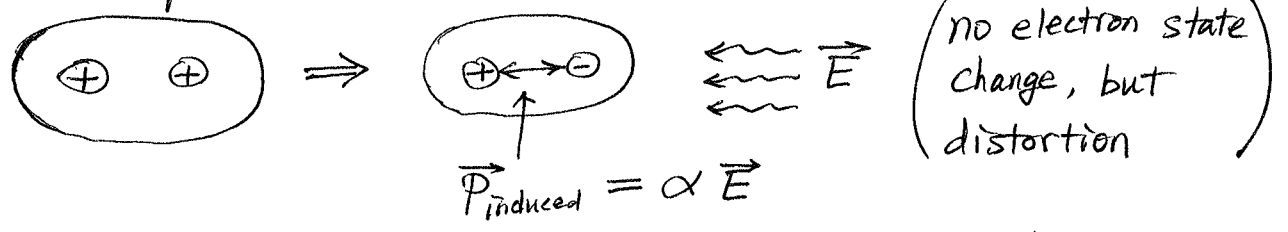
The induced electric dipole $\vec{P}_{induced}$ oscillate with the incident electric field $\Rightarrow$ emit 2nd photon (Scattering)

① Majority case: $\vec{P}_{induced}$ oscillate with incident photon at the same frequency $\Rightarrow$ Rayleigh scattering ($\omega_{scatter} = \omega_L$).

② Lower probability: Vibration and rotation of nuclei affect the oscillation of $\vec{P}_{induced}$:

(a) Take some energy from $\vec{P}_{induced}$ and convert to nuclear vibration/rotation energy $\rightarrow$ emit lower frequency ($\omega_{scatter} < \omega_L$) (Stockes lines)

(b) Give some energy to $\vec{P}_{induced}$ from nuclear vibration/rotation energy $\rightarrow$ emit higher frequency ($\omega_{scatter} > \omega_L$) (anti-Stockes)

Scattering is virtual transition, 2-photon process.

When $\omega_L \approx \omega_0$, single-photon process, like absorption and emission, has much higher probability to happen — electron state change, i.e., real transition.
Then scattering is less likely to happen.



Stockes Raman    Rayleigh    Anti-Stockes Raman
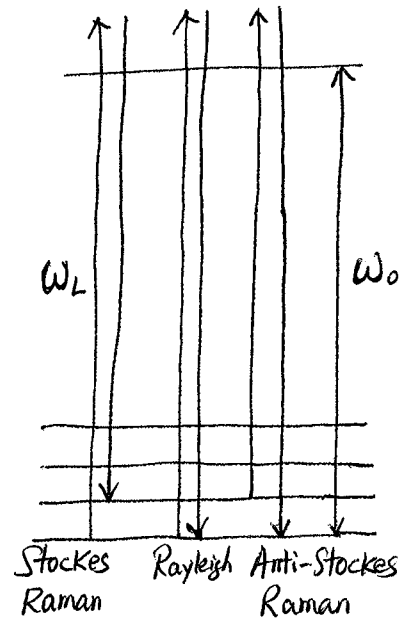
From last lecture we know that

① Atoms do not have permanent electric dipole moment, because $\langle \psi_m | \hat{\vec{D}} | \psi_m \rangle = -e \langle \psi_m | \hat{\vec{r}} | \psi_m \rangle = 0$

② Homonuclear diatomic molecules do not have permanent electric dipole moment, because the molecule's is symmetry and the positive charge center and negative charge center overlaps

$$\langle \psi_e | \hat{\vec{D}} | \psi_e \rangle = \langle \psi_e | 0 | \psi_e \rangle = 0$$

③ Heteronuclear diatomic molecules have nonzero permanent electric dipole moment

$$\langle \psi_e | \hat{\vec{D}} | \psi_e \rangle \neq 0$$

④ Rayleigh and Raman scattering are a two-photon process with the incident photon causing induced electric dipole moment (through electric field) and then the induced dipole moment oscillating with the incident photon electric field to emit the 2nd photon, either at the same frequency as incident photon or at Raman shifted frequency when nuclear vibration and rotation motions affect the oscillation.

⑤ Even without permanent electric dipole moment, atoms and all molecules can have electronic transitions, as when electron state changes, electric dipole moment changes, so the matrix element of the electric dipole moment is non zero:

$$\langle \Psi_n | \overset{\rightarrow}{D} | \Psi_m \rangle \neq 0.$$

⑥ However, without permanent electric dipole moment, the pure rotation spectra (within the same electron state and vibrational state) and the pure vibration–rotation spectra (within the same electron state) can __not__ happen in the homonuclear diatomic molecules. Thus, $N_2$, $O_2$, $H_2$ etc cannot have microwave and infrared spectroscopy.

— This is very important to our Earth enviroment !

BuT as stated in ⑤, $N_2$, $O_2$, $H_2$ etc can still have electronic transitions, thus, visible and UV spectroscopy.