Lecture 8: Fundamentals of Laser Spectroscopy and Molecular Spectra

I. Introduction

* In general, laser remote sensing is an application of laser spectroscopy, which includes the spectroscopy not only between laser and atoms, but also between laser and molecules.
* Today, we will concentrate on the laser spectroscopy with atoms, and also mention something with molecules.
* The fundamentals of QM, atomic structure and atomic transition are the preparation for the spectroscopy.

* Why do we care about the spectroscopy?

  - Spectroscopy is like fingerprints, which can be used to identify species of atoms, molecules, etc.
  - Spectroscopy is also affected by surrounding environment, such as temperature, wind, pressure, so they can serve as good tracers to detect atmosphere, ocean, i.e., environment interested.

* A broadband lidar system, which cannot distinguish the return photon spectrum, may be used for those measurements that depend only on spectral intensity, e.g., Rayleigh, Mie lidar, Resonance fluorescence for density.

* A narrowband lidar system, which can distinguish spectrum, may be used for those measurements that depend on the frequency position and width of a spectral feature, e.g., Doppler lidar (resonance fluorescence and Rayleigh)
II. Laser Spectroscopy

What we concern here is the width and shape of spectral lines from atom and laser (light) interaction.

1. Natural linewidth

The uncertainty principle tells us:

\[ \Delta E \cdot \Delta t = h \quad (4.1) \]

\[ \Rightarrow h \Delta \omega \cdot \Delta t = h \quad \Rightarrow \Delta \omega = \frac{1}{\Delta t} \]

\[ \therefore \Delta \nu = \frac{\Delta \omega}{2\pi} = \frac{1}{2\pi \Delta t} \quad (4.2) \]

It means that those energy levels of an atom, which have finite radiative lifetimes, cannot be considered to be infinitely sharp. The energy level has certain width, given by Eq. (4.2).

The radiative lifetime is defined as below:

Let us consider an assembly of atoms in which \( N_k(0) \) atoms per unit volume are excited in the excited state \( k \) at time \( t=0 \). In general, these atoms will decay by spontaneous emission to a number of lower levels \( i \). In absence of collision depopulation, the population density in level \( k \) decreases at a rate given by:

\[ \frac{dN_k}{dt} = N_k \sum_i A_{ki}, \quad (4.3) \]

where prime indicates that it sums only over those levels that have lower energy than that of \( k \).

\[ \therefore N_k(t) = N_k(0) \exp \left[ -\frac{t}{\tau_k} \right], \quad (4.4) \]

where \( \tau_k = \frac{1}{\sum_i A_{ki}} \) is the radiative lifetime.
The half-width of the energy level \( k \) is determined by the radiative lifetime:

\[
\Gamma_k = \Delta \omega_k = \Delta E_k / h = 1 / T_k = \sum_i' A_{ki} \tag{4.6}
\]

where \( A_{ki} \) are the transition probabilities of the allowed electric dipole transitions from level \( k \) to all possible lower levels, \( i \).

Since in general both the upper and lower levels of an electric dipole transition have finite lifetimes, the uncertainty in the frequency of the emitted photons must include the uncertainty in the energy of both the upper and the lower levels. The frequency distribution of spectral line was obtained \( RM-l_y \) by Weisskopf and Wigner (1930). The result is a Lorentzian curve:

\[
I_{ki}(\omega) = I_0 \frac{\Gamma_{ki}/2\pi}{(\omega - \omega_{ki})^2 + \Gamma_{ki}^2/4} \tag{4.7}
\]

Where \( I_0 \) is the peak intensity,

\[
\text{FWHM} = \Delta \omega_{1/2} = \Gamma_{ki} = \Gamma_k + \Gamma_i = \sum_j A_{kj} + \frac{\sum A_{ki} \chi}{h} \tag{4.8}
\]

Normally, a typical transition has \( \Gamma_k \approx 10^{-5} \text{s} \).

Therefore, the natural linewidth

\[
\Delta \nu_{\text{natural}} = \frac{\Gamma_{ki}}{2\pi} = \frac{10^8}{2\pi} = 16 \text{ MHz}
\]

For Na \( ^2P_{3/2} \), \( T_k = 1.623 \times 10^{-8} \text{s} \), \( \Delta \nu_{\text{natural}}^{\text{Na}} = \frac{1}{2\pi \times 1.623 \times 10^{-8}} \)

For Fe, \( T_k = 6.1 \times 10^{-8} \text{s} \), \( \Rightarrow \Delta \nu_{\text{natural}}^{\text{Fe}} = 2.6 \text{ MHz} \).
2. Collision broadening of spectral lines. (Pressure Broadening)

* Although an isolated atom will emit a spectral line of finite width, in any real source, an atom will be subjected to the interaction forces of neighboring atoms, ions, molecules. These collisions will perturb the state of the radiating atom so lead to a broadening of the line which is often greater than its natural linewidth. This is called collision broadening, also called pressure broadening, as the increase in the linewidth is a function of the density of the perturbing species.

* We do not go in details for this, but the collision's effect is to shorten the radiative lifetime of atom. So a shorter lifetime $\tau$ will be resulted. Then the line-width of the spectral line is still given by $\Gamma = \frac{1}{\tau}$, (4.9)

and the line shape is still a Lorentzian shape:

$$I_{\mathrm{L}}(\omega) = I_0 \frac{\Gamma/2\pi}{(\omega - \omega_L)^2 + (\Gamma/2)^2} \quad (4.10)$$

* Collision of two atoms is the process that these two atoms approach to each other (close enough) and form a temporary molecule, and then separate from each other again. When they get close enough, their energy levels will be changed/shifted. If during this time, transition occurs, the freq. will be shifted and the width will be broadened.

![Diagram of molecular and atomic levels](chart.png)
3. Doppler broadening.

Doppler shift: \( \omega = \omega_0 \left(1 - \frac{v \cdot k}{c} \right) = \omega_0 \left(1 - \frac{v^2}{c^2} \right) \)

Maxwell distribution:
\[
P(v_2) \, dv_2 = \sqrt{\frac{M}{2\pi K_B T}} \exp \left[ -\frac{M v_2^2}{2 K_B T} \right] \, dv_2
\]

Phase velocity:
\[
\nu_2 = \frac{\omega_0 - \omega}{\omega_0 \cdot c} \quad \Rightarrow \quad dv_2 = -\frac{c}{\omega_0} \, dw
\]

\[
P(\omega) \, d\omega \propto P(v_2) \, dv_2
\]
\[
= \sqrt{\frac{M}{2\pi K_B T}} \exp \left[ -\frac{M (\omega_0 - \omega)^2 c^2}{2 \omega_0^2 K_B T} \right] \cdot \frac{c}{\omega_0} \, d\omega
\]

Let \( \sigma = \sqrt{\frac{\omega_0^2 K_B T}{M c^2}} = \frac{\omega_0}{c} \sqrt{\frac{K_B T}{M}} \)

\[
P(\omega) \, d\omega = \frac{1}{\sqrt{2\pi} \sigma} \exp \left[ -\frac{(\omega_0 - \omega)^2}{2 \sigma^2} \right] \, d\omega
\]

This is called Doppler broadening.

Notice that the Doppler shift is a function of radial velocity while the Doppler broadening is a function of temperature. This is the basis for Doppler lidars to measure wind and temp.

*Comparison of Gaussian shape with Lorentzian shape.*
Examples of Doppler broadening:

Na

Fe

K
4. Classification of Broadening

Among the broadening discussed above, there are two different types of broadening: the homogeneous broadening and the inhomogeneous broadening.

(i) Homogeneous broadening: natural linewidth, collision broadening, and saturation broadening. Essentially, they are caused by limited radiative lifetime of atoms. So, they can be represented by an effective lifetime $\tau$, and $I = \frac{l}{\tau}$.

The lineshape is a Lorentzian function:

$$I(\omega) = I_0 \frac{\Gamma/\pi}{(\omega - \omega_0)^2 + (\Gamma/2)^2}$$

$$\therefore \Delta \omega_{\text{FWHM}} = \Gamma = \frac{l}{\tau}; \text{ same for all atoms.}$$

(ii) Inhomogeneous broadening: Doppler broadening. Essentially, they are caused by the different central frequency shifts of different atoms. The overall lineshape is a superposition of the different spectral lines from different atoms. Therefore, inhomogeneous.

When atoms' motions are random, the lineshape is given by a Gaussian function:

$$I(\omega) = \frac{I_0}{\sqrt{2\pi} \sigma} \exp \left[-\frac{(\omega - \omega_0)^2}{2\sigma^2}\right]$$

Where $\sigma$ is the rms width of the Gaussian peak.

$$\text{FWHM} = \sigma \sqrt{8 \ln 2}.$$. 
5. Voigt Integration (Voigt Shape)

The different broadenings may present at the same time, e.g., when we have Doppler broadening, we also have the natural linewidth of each spectral line. So, the overall lineshape is a convolution of these two lineshapes:

\[ \mathcal{G}(\omega) = \int_{-\infty}^{\infty} L(\omega - \omega') \mathcal{G}(\omega', \omega) \, d\omega', \]

where \( L(\omega) \) is the Lorentzian lineshape for natural linewidth,
and \( \mathcal{G}(\omega) \) is the Gaussian shape for Doppler broadening.

\[ \mathcal{G}(\omega) = C \int_{-\infty}^{+\infty} \exp \left[ - \frac{(\omega - \omega')^2}{2\sigma^2} \right] \frac{1}{(\omega - \omega') + (\gamma/2)} \, d\omega', \]

where \( C \) is the normalization factor.

This shape is called Voigt shape.

This integration is called Voigt integration, which is a convolution of Lorentzian and Gaussian shapes. There is no analytical solution to it.

* Usually, the Lorentzian width \( \Gamma \) is much smaller than the Doppler width \( \sigma \): \( \Gamma << \sigma \),
then the Lorentzian width can be neglected, or say Lorentzian shape as a \( \sigma \) function. Thus, we get a pure Gaussian shape: \( \mathcal{G}(\omega) = C \exp \left[ - \frac{(\omega - \omega')^2}{2\sigma^2} \right] \).

⇒ This is called Doppler limit.
6. Effect of instrumental shape or laser shape

Above spectral lineshape was derived under the assumption that the instrument or laser we used to measure the spectral lines have infinite small spectral width (i.e., a $\delta$ function). But in reality, any instrument or laser has finite spectral width. Therefore, the observed spectral line will have the influence from the instrumental profile.

* The overall observed spectral lineshape will be a convolution of the intrinsic atomic/molecular spectral lineshape with the instrumental/laser lineshape.

$$g_\text{f}(w) = \int_{-\infty}^{+\infty} g_\text{A}(w',w) g_\text{L}(w-w') dw'$$

Where $g_\text{A}(w)$ is the intrinsic spectral distribution of the atom, and $g_\text{L}(w)$ is the spectral distribution of the laser.

* If both distributions can be represented by Gaussian shapes with rms widths of $\sigma_1$ and $\sigma_2$, then the convoluted lineshape will be still a Gaussian distribution, with a new rms width

$$\sigma = \sqrt{\sigma_1^2 + \sigma_2^2}.$$
7. Saturation and Saturation Broadening

When radiation (laser) frequency is in resonance with an atomic transition, absorption will occur. Sometimes, an absorption coefficient $\alpha$ is used to describe an atomic system's effect on the incident laser light through absorption. $\alpha$ is defined as

$$dI = -I\alpha dx,$$
where $I$ is light intensity.

$$\Rightarrow I(x) = I_0 e^{-\alpha x}$$

The absorption coefficient $\alpha (m^{-1})$ is a constant in classical physics, and a linear absorption relationship.

* However, when incident laser light is strong, the atomic absorption coefficient is not a constant anymore, but decreases gradually. This change in absorption coefficient is called "saturation".

* The saturation phenomenon can be explained using Einstein theory.

$$N_1 + N_2 = N_0$$
for a 2-energy level system.

When no laser radiation, $N_2 = 0, N_1 = N_0$.

When laser is acting on the atomic system, three processes will happen: absorption, stimulated emission, and spontaneous emission. A population rate equation can be written as

$$-\frac{dN_1}{dt} = \frac{dN_2}{dt} = N_1 \int B_{12} g(\omega) P(\omega) d\omega$$

$$- N_2 \int B_{21} g(\omega) P(\omega) d\omega - N_2 A_{21}$$

$$= N_1 B_{12} g(\omega) P - N_2 B_{21} g(\omega) P - N_2 A_{21}.$$
When reaching steady state, we have \( \frac{dN_1}{dt} = \frac{dN_2}{dt} = 0 \)

\[
N_1 - N_2 = -\frac{A_{21}}{2B \rho g_A(\omega) + A_{21}} N_0 = \frac{1}{1 + S} N_0,
\]
where \( B = B_{12} = B_{21} \) (ignoring degeneracy),

\[S = \frac{2 B_{12} g_A(\omega)}{A_{21}} \text{ (saturation factor)}\]

When laser intensity increases,

\[\Rightarrow \text{ \emph{W}st = } B \rho g_A(\omega) \text{ increases}\]
\[\Rightarrow N_2 \text{ on the upper level can not be neglected anymore}\]
\[\Rightarrow \text{the absorption amount of light } \propto (N_1 - N_2)\]
\[\Rightarrow \alpha \text{ will decrease: } \alpha = \frac{1}{1 + S} \alpha', \quad [\alpha' = \alpha (S = 0)]\]

* Saturation Broadening

\[\alpha = \frac{1}{1 + S} \alpha', \quad S = \frac{2B_{12} g_A(\omega)}{A_{21}}\]

\( g_A(\omega) \) is the absorption lineshape of the atom.

\( S \) is a function of frequency:
- at \( \omega = \omega_0 \), \( g_A(\omega) \) is max \( \rightarrow S \) is max, strong saturation
- at wing, \( g_A(\omega) \) is small \( \rightarrow S \) is small, less saturation

\[\Rightarrow \text{the lineshape } \Rightarrow \text{ flatter } \Rightarrow \text{ broadening}\]

For Lorentzian shape (homogeneous),

\[\alpha = \alpha_0 \frac{(\gamma/2)^2}{(\omega - \omega_0)^2 + (1 + S)(\gamma/2)^2}\]

where \[S = \frac{4B \rho}{\pi A_{21}} \text{ (saturation factor)} \Rightarrow \Delta \omega = \sqrt{1 + S} \gamma\]
§ Saturation–absorption Spectroscopy

* For inhomogeneous broadened spectral lines, the saturation effect will occur only on the group of atoms that interact with the laser light. Therefore, a dip will occur in the atomic speed distribution on lower energy level.

\[ w = w_0 \left( 1 + \frac{\nu'}{c} \right) \]

This is called Bennett Hole Effect.

Understanding of this: for certain freq of laser, the laser photons only interact with certain group of atoms whose radial velocity could allow the Doppler Shift of the laser freq. Moving on to the resonance freq of atomic absorption line.

Thus, when laser intensity is strong enough, there will be some population staying on the upper level (dynamical equilibrium), resulting in a hole on the ground level population.

* Note that this dip or peak is basically the natural linewidth, so it's Doppler-free, with width much much narrower than the Doppler width. Such spectrum can be used to lock laser frequency and calibrate laser frequency.

* This is a technique used in Na and K lidars.
We don't measure the speed distribution directly, but measure either the transmitted light or fluorescence light intensity.

We prefer the fluorescence method, because of the better SNR.

If we use only one beam of laser and scan its freq through the atomic absorption line, we won't see the "hole", because the line will drop at every frequency.

But if we use one strong laser to saturate (i.e., burn a hole) the atoms, and then use another weak laser to scan through the absorption line, we will be able to see the hole. — "Strong light saturate, and weak light detect in the opposite direction".

An equivalent method is the dual-beam equal intensity method used in the Na or K lidars.
To understand this
saturation-absorption spectrum,
let us use a 3-energy level system.

Optical pumping effect.
Molecular Spectra

A molecule consists of several atoms.

inner electrons — no change
1. outer electrons → form intermolecular bond
2. vibration around a balance point
3. whole molecule rotates around axes.

<table>
<thead>
<tr>
<th>Motion</th>
<th>Transition Frequency</th>
<th>Energy (eV)</th>
<th>Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic State</td>
<td>UV or Visible</td>
<td>1-20</td>
<td>electronic spectra</td>
</tr>
<tr>
<td>Molecular Vibration</td>
<td>near infrared</td>
<td>0.05-1</td>
<td>Rotation-vibration spectra</td>
</tr>
<tr>
<td>Molecular Rotation</td>
<td>far infrared and microwave</td>
<td>10^{-4}-0.05</td>
<td>Rotation spectra</td>
</tr>
</tbody>
</table>

In a first approximation, the energy of a molecule can be represented as the sum of three parts—the electronic, the vibrational, and the rotational energy:

\[ E = E_e + E_v + E_r. \] (1)

In Fig. 10 the vibrational and rotational levels in two electronic states are represented schematically.

Fig. 10. 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.