Lecture 6

Basics of gaseous absorption/emission. Line shapes.

Objectives:
1. Basics of atomic and molecular absorption/emission spectra.
2. Spectral line shapes: Lorentz profile, Doppler profile and Voigt profile

Required reading:
L02: 1.3

Recommended/advanced reading:

1. Basics of atomic and molecular absorption/emission spectra

Atomic absorption/emission spectra.
- Radiation emission (absorption) occurs only when an electron makes a transition from one state with energy $E_k$ to a state with lower (higher) energy $E_j$:

  \[ E_k - E_j = h\nu \]

Figure 6.1 Absorption/Emission processes

Bohr’s model of a hydrogen atom:
- The energy level is given as

  \[ E_n = -\frac{R_H \hbar c}{n^2} \quad , \quad n=1,2,3,\ldots \quad [6.1] \]

where $R_H$ is the Ryberg constant (=1.092x10^5 cm⁻¹ for hydrogen); $\hbar$ is the Planck’s constant, and $c$ is the speed of light.
The wavenumber of emission/absorption lines of hydrogen atom:

\[
\nu = R_H \left( \frac{1}{j^2} - \frac{1}{k^2} \right)
\]  [6.2]

where \( j \) and \( k \) are integers defining the lower and higher energy levels, respectively.

**Figure 6.2** Energy level diagram for the hydrogen atom.
Molecular Absorption/Emission Spectra

Molecular absorption spectrum is substantially more complicated than that of an atom because molecules have several forms of internal energy. This is the subject of spectroscopy and quantum theory.

Three types of absorption/emission spectra:

i) Sharp lines of finite widths
ii) Aggregations (series) of lines called bands;
iii) Spectral continuum extending over a broad range of wavelengths
Figure 6.4 Concept of a line, band, and continuous spectra
**Main underlying physical principles of molecular absorption/emission:**

1) The origins of absorption/emission lie in exchanges of energy between gas molecules and electromagnetic field.

2) In general, total energy of a molecule can be given as:

\[ E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + E_{\text{tr}} \]

- \( E_{\text{rot}} \) is the kinetic energy of rotation (energy of the rotation of a molecule as a unit body): about 1-500 cm\(^{-1}\) (far-infrared to microwave region)
- \( E_{\text{vib}} \) is the kinetic energy of vibration: energy of vibrating nuclei about their equilibrium positions; about 500 to 10\(^4\) cm\(^{-1}\) (near- to far-IR)
- \( E_{\text{el}} \) is the electronic energy: potential energy of electron arrangement; about 10\(^4\)-10\(^5\) cm\(^{-1}\) (UV and visible)
- \( E_{\text{tr}} \) is translation energy: exchange of kinetic energy between the molecules during collisions; about 400 cm\(^{-1}\) for T =300 K

- From \( E_{\text{rot}} < E_{\text{tr}} < E_{\text{vib}} < E_{\text{el}} \) follows that:
  
  i) Rotational energy change will accompany a vibrational transition. Therefore, vibration-rotation bands are often formed.
  
  ii) Kinetic collision, by changing the translation energy, influence rotational levels strongly, vibrational levels slightly, and electronic levels scarcely at all.

- **Energy** \( E_{\text{rot}}, E_{\text{vib}}, \text{ and } E_{\text{el}} \) **are quantized** and have only discrete values specified by one or more **quantum numbers** (see below). Not all transitions between quantized energy level are allowed - they are subject to selection rules.

3) Radiative transitions of purely rotational energy require that a molecule possess a permanent electrical or magnetic dipole moment.

**NOTE:** A **dipole** is represented by centers of positive and negative charges \( Q \) separated by a distance \( d \): the dipole moment = \( Q \cdot d \)
Table 6.1 Atmospheric molecule structure and dipole moment status (see also Table 5.3)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Structure</th>
<th>Permanent dipole moment</th>
<th>May acquire dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>N - N</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>O₂</td>
<td>O - O</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>CO</td>
<td>C - O</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>CO₂</td>
<td>O - C - O</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>(in two vibrational modes)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂O</td>
<td>N - N - O</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>H₂O</td>
<td>H - O - H</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>O₃</td>
<td>O - O - O</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>CH₄</td>
<td>H - C - H</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>(in two vibrational modes)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**NOTE:** If charges are distributed symmetrically => no permanent dipole moment => no radiative activity in the far-infrared (i.e., no transitions in rotational energy)

**Example:** homonuclear diatomic molecules (N₂, O₂);

**NOTE:** CO₂ and CH₄ don’t have permanent dipole moment => no pure rotational transitions. But they can acquire the oscillating dipole moments in their vibrational modes => have vibration-rotation bands

**NOTE:** CO, N₂O, H₂O and O₃ exhibit pure rotational spectra.
4) Radiative transitions of vibrational energy require a change in the dipole moment (i.e., oscillating moment)

**Figure 6.5** Vibrational modes of diatomic and triatomic atmospheric molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Vibrational Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>no vibrational transition (symmetric stretching mode)</td>
</tr>
<tr>
<td>O₂</td>
<td>single vibrational mode</td>
</tr>
<tr>
<td>CO</td>
<td>ν₁ (symmetric stretching mode =&gt; radiatively inactive)</td>
</tr>
<tr>
<td></td>
<td>ν₂α two bending modes have same energy</td>
</tr>
<tr>
<td></td>
<td>ν₂β (degenerated modes)</td>
</tr>
<tr>
<td>CO₂</td>
<td>ν₃ (asymmetric stretching mode =&gt; radiatively active)</td>
</tr>
</tbody>
</table>

**NOTE:** Homonuclear diatomic molecules N₂ and O₂ don’t have neither rotational nor vibrational transitions (because of their symmetrical structures) => no radiative activity in the infrared. But these molecules become radiatively active in UV.

**NOTE:** The number of independent vibrational modes (called **normal modes**) of a molecule with N>2 atoms are 3N-6 for non-linear molecules and 3N-5 for a linear molecule.

**NOTE:** Both H₂O and O₃ have three normal band ν₁, ν₂ and ν₃: all are optically active.

**NOTE:** CH₄ has nine normal modes but only ν₃ and ν₄ are active in IR.
5) Rotational –vibrational transitions:

*Pure rotational transitions* can be understood by evoking the notion of a rigid quantized rotator.

<table>
<thead>
<tr>
<th>Linear diatomic: O₂, CO, NO</th>
<th>Linear triatomic: CO₂, N₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 degrees of rotational freedom and 2 equal moments of inertia</td>
<td>3 degrees of rotational freedom and 3 unequal moments of inertia</td>
</tr>
</tbody>
</table>

**Figure 6.6** Axes of rotational freedom for linear and asymmetric top molecules.
Let’s consider a diatomic molecule with masses $m_1$ and $m_2$ at distances $r_1$ and $r_2$ from their common center of gravity. The moment of inertia of this two-mass rigid rotator is

$$I_m = m_1r_1^2 + m_2r_2^2$$

If $r$ is the distance between the atoms, we have

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \text{and} \quad r_2 = \frac{m_1}{m_1 + m_2} r$$

Introducing the reduced mass $m'$ as

$$m' = \frac{m_1 m_2}{m_1 + m_2}$$

we have

$$I_m = \frac{m_1 m_2}{m_1 + m_2} r^2 = m' r^2$$

The angular momentum $L$ of a rigid rotator is defined as

$$L = I_m \omega = m' r^2 \omega$$

where $\omega$ is the angular velocity (rad sec$^{-1}$)

The kinetic energy of a rotator is equal

$$E_{rot} = \frac{1}{2} L \omega = \frac{1}{2} I_m \omega^2$$

**Classic rotator**: both angular momentum and rotational kinetic energy are continues

**Quantized rotator**: Quantum restrictions on rotational energy as a consequence of the quantum restrictions on angular momentum (which found from a solution of the Schroedinger equation).

The quantum restrictions on angular momentum are

$$I_m \omega = \frac{\hbar}{2\pi} [J(J + 1)]^{1/2}$$

$J$ is the **rotational quantum number**: $J = 0, 1, 2, 3…$

$h$ is the Planck’s constant.

Thus we have
\[ E_{\text{rot}} = \frac{1}{2} I_m \omega^2 = \frac{1}{2} \left( \frac{I_m \omega}{I_m} \right)^2 = \frac{\hbar^2}{8\pi^2 I_m} J(J + 1) \]

or

\[ E_J = B \ h \ c \ J(J+1) \quad [6.3] \]

\( B \) is the rotational constant and it depends on the moments of inertia \( I_m \) of a given molecule as

\[ B = \frac{\hbar}{8\pi^2 c I_m} \]

Units of \( B \): LENGTH\(^{-1} \)

**Selection rules:** \( \Delta J = 1 \) for absorption and \( \Delta J = -1 \) for emission

Consider rotational transition between the upper energy level \( E' \) and lower energy level \( E'' \). We have for upper level \( E' = B \ h \ c \ J'(J'+1) \) and for lower level \( E'' = B \ h \ c \ J''(J''+1) \). Thus

\[ \Delta E_J = B \ h \ c \ (J''+1) = B \ h \ c \ J' \]

Recalling that \( \Delta E_J = \nu \ h \ c \), position of a pure rotational line is given by

\[ \nu = 2 \ B \ J' \quad (\text{cm}^{-1}) \]

=> equally spaced lines because \( B \) is constant for a given molecule

**NOTE:** The nonlinear molecules \( \text{H}_2\text{O} \) and \( \text{O}_3 \), asymmetric tops with three moments of inertia, give very complex spectra.
**Pure vibrational energy:**

Similar to the derivation above, one can introduce a classical vibrator (whose energies are continuous) and then apply the quantum restrictions from the Schroedinger equation.

The allowed energy levels are

\[
E_{vk} = h c \nu_k (v_k +1/2)
\]  

[6.4]

where \( \nu_k \) is the wavenumber of the k-normal vibrational mode;

\( \nu_k \) is the **vibrational quantum number**; \( \nu_k = 0, 1, 2, 3… \)

For pure vibrational transition, we have \( \Delta E = h \nu_k \)

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**Combine vibrational-rotational energy:**

\[
E_{j,v} = B h c J (J+1)+ h c \nu_k (v_k +1/2)
\]  

[6.5]

- Because \( E_{vib} > E_{rot} \), the spectrum of the combined transitions is a series of rotational lines grouped around the vibrational wavenumber:

  For \( \Delta J = +1 \) we have \( \nu = \nu_k (2B J'), J' = 1, 2, 3… \)

  For \( \Delta J = -1 \) we have \( \nu = \nu_k (-2B (J'+1)), J' = 0, 1, 2, 3… \)

where \( J' \) is the rotational quantum number in the excited vibrational state \( \nu_k \).
Figure 6.6 Simultaneous transitions in vibrational and rotational energies. (* denotes lower energy level and ′ denotes upper energy level).

NOTE:
P-branch is the rotational transitions following the selection rule $\Delta J = -1$
Q-branch is the rotational transitions following the selection rule $\Delta J = 0$
R-branch is the rotational transitions following the selection rule $\Delta J = 1$
2. Spectral line shapes: Lorentz profile, Doppler profile, and Voigt profile.

Three main properties that define an absorption line: central position of the line (e.g., the central frequency \( \nu_0 \) or the central wavenumber \( \nu' \)), strength of the line (or intensity, \( S \)), and shape factor (or line profile, \( f \)) of the line.

- Each line has a finite width (referred to as **natural broadening of a spectral line**).
- In the atmosphere, several processes may result in an additional broadening of a spectral line of the molecules: 1) collisions between molecules (referred to as the **pressure broadening**); 2) due to the differences in the molecule thermal velocities (referred to as the **Doppler broadening**); and 3) the combination of the above processes.

**Lorentz profile** of a spectral line is used to characterize the **pressure broadening** and is defined as:

\[
    f_L(\nu - \nu_0) = \frac{\alpha}{\pi} \frac{\nu}{(\nu - \nu_0)^2 + \alpha^2}
\]

where \( f(\nu - \nu_0) \) is the shape factor of a spectral line;

\( \nu_0 \) is the wavenumber of a central position of a line;

\( \alpha \) is the half-width of a line at the half maximum (in cm\(^{-1}\)), (often called the **line width**)

- The **half-width** of the Lorentz line shape is a function of pressure \( P \) and temperature \( T \) and can be expressed as

\[
    \alpha(P, T) = \alpha_0 \left( \frac{P}{P_0} \left( \frac{T_0}{T} \right)^n \right)
\]

where \( \alpha_0 \) is the reference half-width for STP: \( T_0 = 273K; P = 1013 \text{ mb} \).

\( \alpha_0 \) is in the range from about 0.01 to 0.1 cm\(^{-1}\) for most atmospheric radiatively active gases.

For most gases \( n=1/2 \)
NOTE: The above dependence on pressure is very important because atmospheric pressure varies by an order of 3 from the surface to about 40 km.

- The **Lorentz profile** is fundamental in the radiative transfer in the lower atmosphere where the pressure is high.
- The collisions between like molecules (**self-broadening**) produces the large line-widths than do collisions between unlike molecules (**foreign broadening**). Because radiatively active gases have low concentrations, the **foreign broadening** often dominates in infrared radiative transfer.

**Doppler profile** is defined in the absence of collision effects (i.e., pressure broadening) as:

\[
\alpha_D = \frac{V_0}{c} (2k_B T / m)^{1/2}
\]

where \( c \) is the speed of light; \( k_B \) is the Boltzmann’s constant, \( m \) is the mass of the molecule.

The Doppler half-width at the half maximum is \( \alpha_D (1n2)^{1/2} \)

NOTE: The Doppler effect comes from random molecular motions. If the molecule moves with the thermal velocity \( V \) and emits at the frequency \( \nu_0 \), it would appear that it emits at the frequency \( \tilde{\nu} = \nu_0 \left(1 \pm \frac{V}{c}\right) \), where \( c \) is the speed of light and \( V \ll c \).

✓ The Doppler broadening is important at the altitudes from about 20 to 50 km.
Figure 6.7 Comparison of the Doppler and Lorentz profiles for equivalent line strengths and widths.

**NOTE:** Line wings are more strongly affected by pressure than Doppler broadening.

_Voigt profile_ is the combination of the Lorentz and Doppler profiles to characterize broadening under the low-pressure conditions (above about 40 km in the atmosphere). (i.e., it is required because the collisions (pressure broadening) and Doppler effect can not be treated as completely independent processes:

\[
\begin{align*}
    f_{\text{Voigt}}(v - v_0) &= \int_{-\infty}^{\infty} f_L(v' - v_0) f_D(v - v') dv' = \\
    \frac{\alpha}{\alpha_D \pi^{3/2}} \int_{-\infty}^{\infty} \frac{1}{(v' - v_0')^2 + \alpha^2} \exp \left[ -\left( \frac{v - v'}{\alpha_D} \right)^2 \right] dv' \\
    \text{[6.8]} 
\end{align*}
\]

**NOTE:** The Voigt profile requires numerical calculations.
Nature of the Voigt profile:

- **At high pressure**: the Doppler profile is narrow compared to the Lorentz profile so under these conditions the Voigt profile is the same as Lorentz profile.

- **At low pressure**: the behavior is more complicated – a kind of hybrid line with a Doppler center but with Lorentz wings.