

Lecture 6

Absorption and emission by atmospheric gases

1. Properties of atmospheric gases
2. Basic principles of molecular emission/absorption

Required reading:

S: 3.1-.32

Suggested reading:

Liou 3.2

1. Properties of atmospheric gases.

- ✓ Atmospheric gases are highly selective in their ability to absorb and emit radiation. Each radiatively active gas has a specific absorption spectrum – its own signature.
- ✓ An atmosphere is the mixture of gases and thus the abundance of gases in the atmosphere controls the overall spectral absorption.
- ✓ Radiatively active gases in the Earth's atmosphere are highly variable in space and time.
- ✓ The ability of a molecule to absorb (emit) radiation is determined by its structure which controls whether the molecule has a dipole.
 - Structure of molecules: is important for understanding energy forms and the ability of a molecule to absorb/emit radiation:

Based on their geometric structure, molecules can be divided into four types

- Linear molecules (CO_2 , N_2O ; C_2H_2 , all diatomic molecules (e.g., O_2 , N_2 , etc))
- Symmetric top molecules (NH_3 , CH_3Cl)
- Spherical symmetric top molecules (CH_4)
- Asymmetric top molecules (H_2O , O_3):

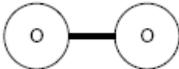
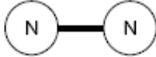
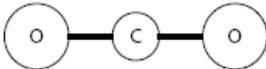
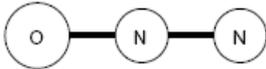
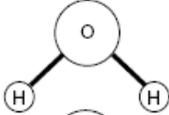
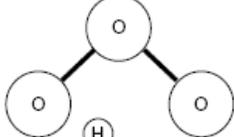
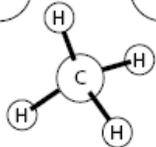
<i>Molecule</i>	<i>Structure</i>		<i>Permanent Electric Dipole Moment?</i>	<i>May acquire dipole moment</i>
Oxygen		linear	No (magnetic dipole)	No
Nitrogen		linear	No	No
Carbon Monoxide		linear	Yes	Yes
Carbon Dioxide		linear	No	Yes
Nitrous Oxide		linear	Yes	Yes
Water		asymmetric top	Yes	Yes
Ozone		asymmetric top	Yes	Yes
Methane		spherical top	Yes	Yes

Figure 6.1 Molecular structures of key atmospheric gases and the dipole moment status.

Rotational and vibrational motions of the molecules:

- *Molecules as a rigid quantized rotator:*

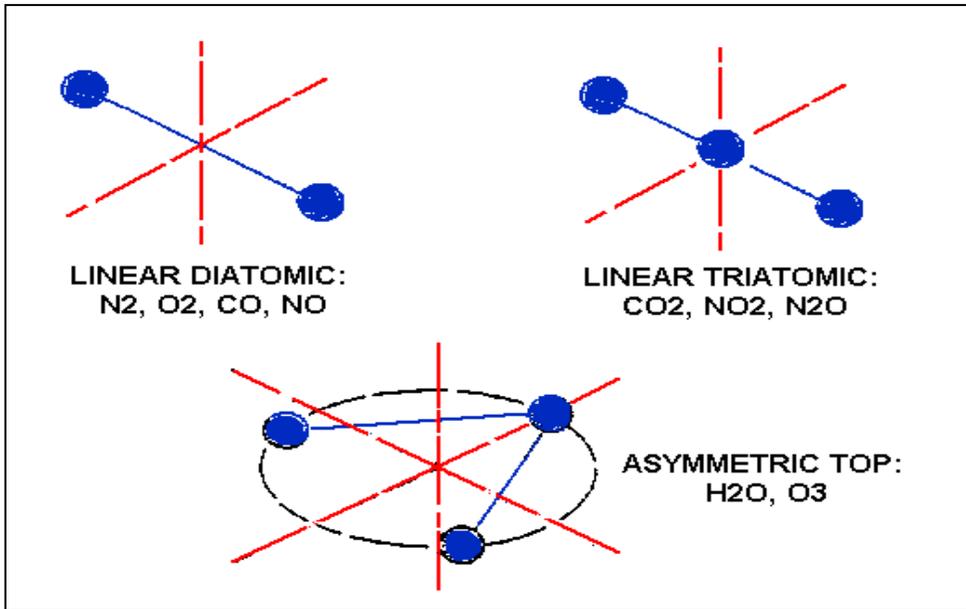


Figure 6.2 Axes (in red) of rotational freedom for linear (2 degrees of rotational freedom and 2 equal moments of inertia) and asymmetric top molecules (3 degrees of rotational freedom and 3 unequal moments of inertia => H₂O and O₃ have very complex spectra

- *Molecules as a quantized vibrator:*

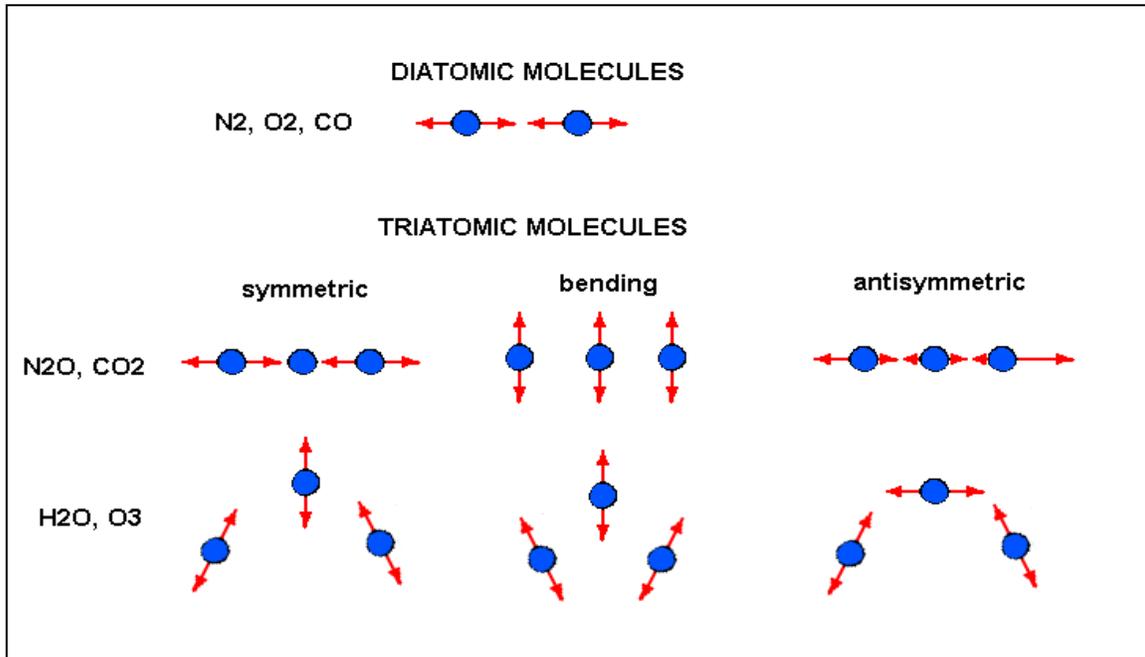


Figure 6.3 Vibrational modes of diatomic and triatomic atmospheric molecules.

2. Basic principles of molecular emission/absorption

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 represented as:

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

E_{rot} is the kinetic energy of rotation (energy of the rotation of a molecule as a unit body): about $1\text{-}500\text{ cm}^{-1}$ (far-infrared to microwave region)

E_{vib} is the kinetic energy of vibration: energy of vibrating atom about their equilibrium positions; about $500\text{ to }10^4\text{ cm}^{-1}$ (near- to far-IR)

E_{el} is the electronic energy: potential energy of electron arrangement; about $10^4\text{-}10^5\text{ cm}^{-1}$ (UV and visible)

E_{tr} is translation energy: exchange of kinetic energy between the molecules during collisions; about 400 cm^{-1} for $T = 300\text{ K}$

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

- **Energy E_{rot} , E_{vib} , and E_{el} are quantized** and have only discrete values specified by one or more **quantum numbers**. 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.

- 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 (N_2 , O_2);

- O_2 has a weak permanent magnetic dipole and thus has a rotational transition in microwave.
- CO , N_2O , H_2O and O_3 exhibit pure rotational spectra because they all have the permanent dipoles.
- CO_2 and CH_4 don't have permanent dipole moment \Rightarrow no pure rotational transitions. But they can acquire the oscillating dipole moments in their vibrational modes \Rightarrow have vibration-rotation bands

4) Radiative transitions of vibrational energy require a change in the dipole moment (i.e., oscillating moment)

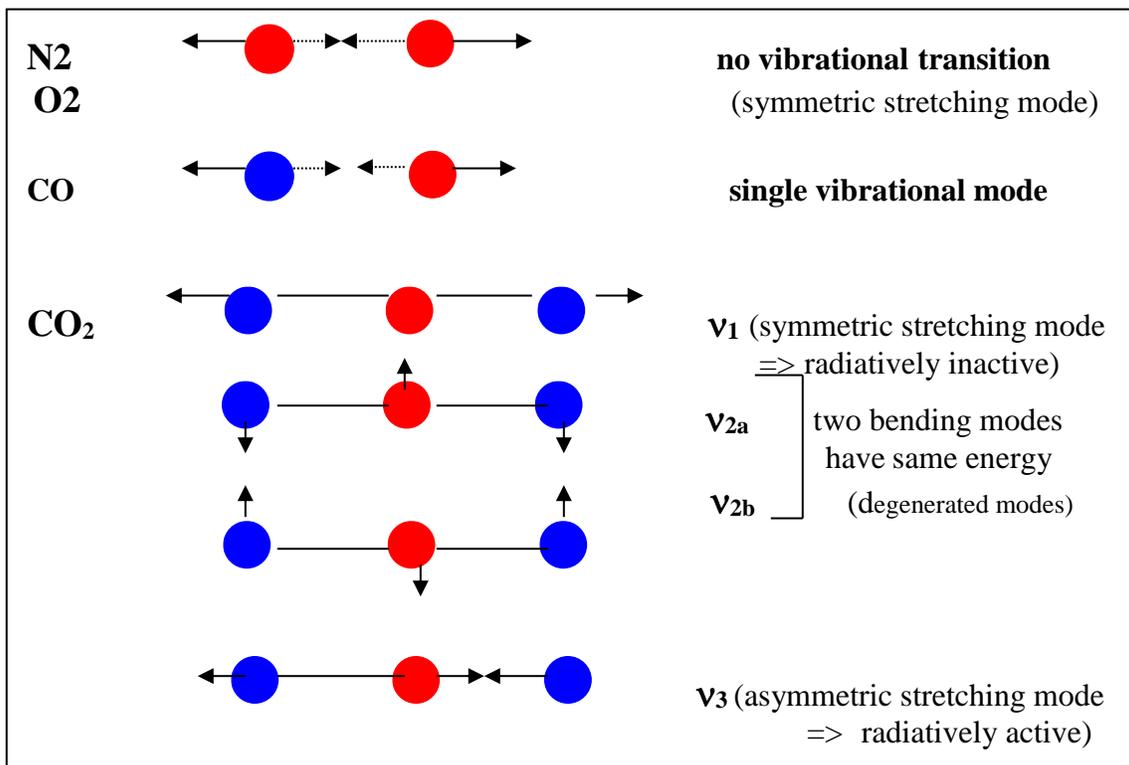


Figure 6.4 Vibrational modes of diatomic and triatomic atmospheric molecules (also Figure 6.3)

NOTE: Homonuclear diatomic molecules N_2 and O_2 don't have neither rotational nor vibrational transitions (because of their symmetrical structures) \Rightarrow no radiative activity in the infrared. But these molecules become radiatively active in UV.

NOTE: The number of independent vibrational modes of a molecule with $N > 2$ atoms are $3N - 6$ for non-linear molecules and $3N - 5$ for a linear molecule. Both **H₂O** and **O₃** have three normal band ν_1 , ν_2 and ν_3 : all are optically active.

CH₄ has nine normal modes but only ν_3 and ν_4 are active in IR.

5) Electronic transitions

- **Electrons on inner orbits** (close to the atomic nucleus) can be disturbed or dislodged only by photons having the large energies (short-wave UV and X-rays);
- **Electrons on the outermost orbits** can be disturbed by the photons having the energies of UV and visible radiation => these electrons are involved in absorption/emission in the UV and visible.
- Both an atom and a molecule can have the **electronic transitions**. Electronic transitions of a molecule are always accompanied by vibrational and rotational transitions and are governed by numerous selection rules.