THE UNIVERSITY OF UTAH

ATMOS 5140
Lecture 11 – Chapter 9

- Absorption by Atmospheric Gases
  - Rotational
  - Vibrational
  - Applications

Basis for Molecular Absorption/Emission

- Changes in the translational kinetic energy of molecules (i.e. temperature)
- Changes in the rotational kinetic energy of polyatomic molecules
- Changes in the vibrational energy of polyatomic molecules
- Changes in the distribution of electric charges within a molecule, possibly including the complete separation (or reunification) of two components previously bound by electrostatic forces

Basis for Molecular Absorption/Emission

Unquantized

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Basis for Molecular Absorption/Emission

Unquantized

- Changes in the translational kinetic energy of molecules (i.e. temperature)

Molecule of smaller Immediate consequence

- Changes in the rotational kinetic energy of polyatomic molecules
- Changes in the vibrational energy of polyatomic molecules
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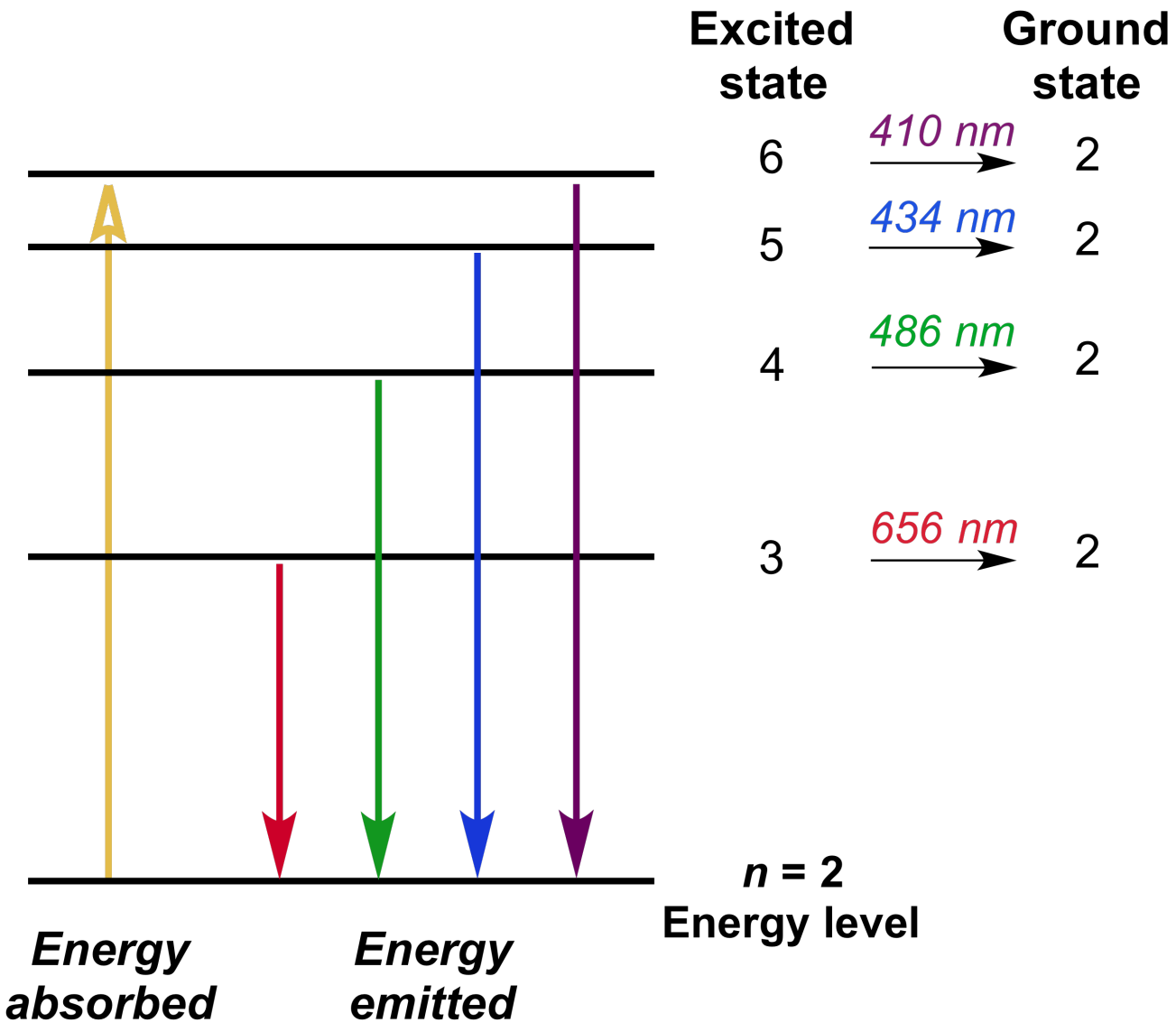
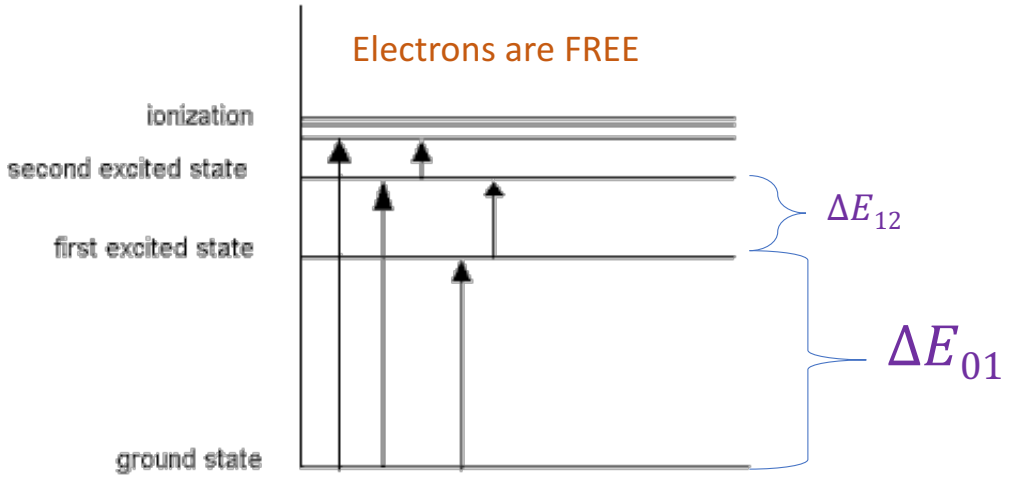

Excited state
Ground state
6
5
4
3
2
2
2
2
410 nm
434 nm
486 nm
656 nm
n = 2
Energy level
Energy absorbed
Energy emitted

Relationship between energy level transitions and absorption/emission line spectrum

$$\lambda = \frac{c}{\nu} = \frac{hc}{\Delta E}$$



For example, if

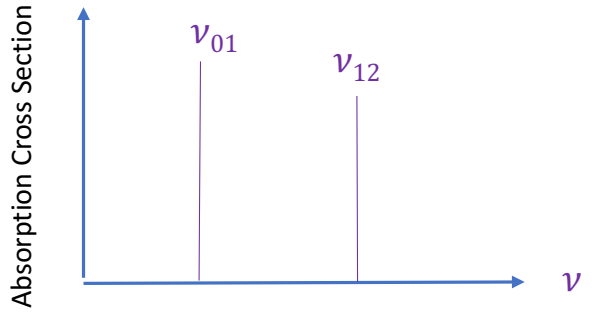
$$\Delta E_{12} = \Delta E_{23}$$

Then

$$\nu_{12} = \nu_{23}$$

DEGENERATE – 2 lines collapsed onto 1

Thus lines are stronger..



Relationship between energy level transitions and absorption/emission line spectrum

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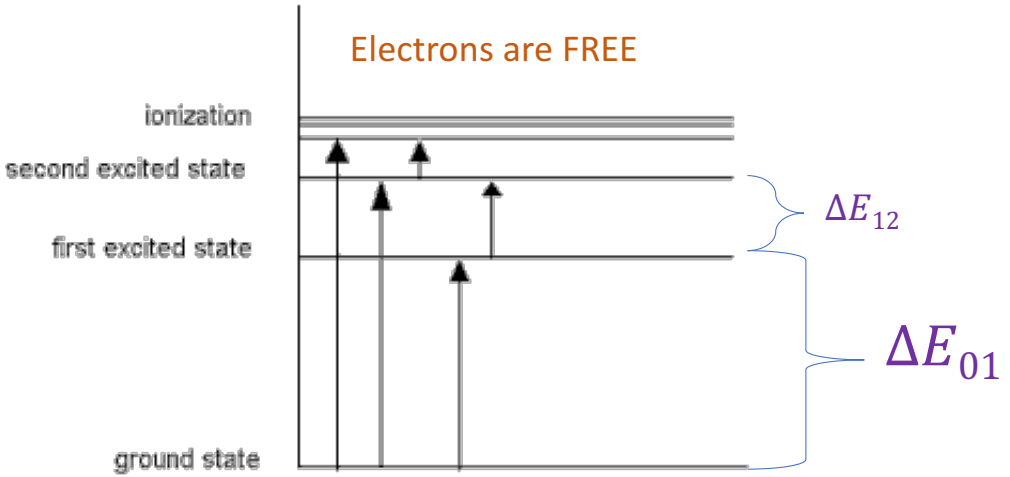
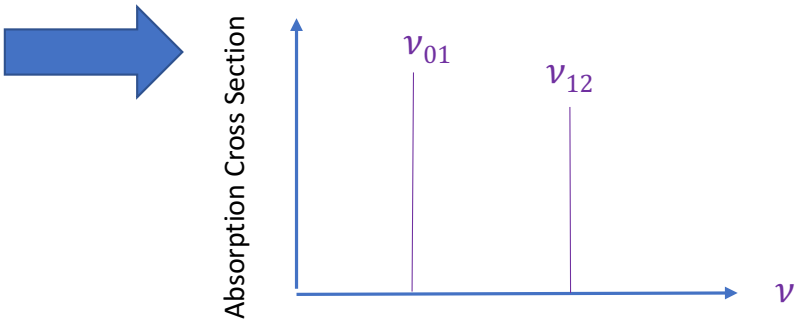


Relative Strengths of the lines:

1. Fraction of molecules in particular state required for transition
2. Likelihood photon has right energy and will encounter molecule in required energy state



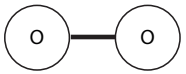
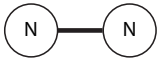
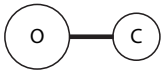
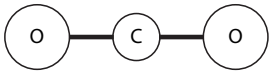
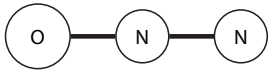
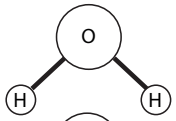
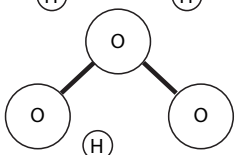
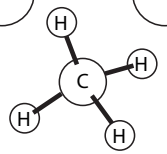
MOST IMPORTANT SLIDE

Energy	Wavelength	Band	Dominant Transition
Lower Energy	> 20 um	Far IR, Microwave	Rotation
	1um – 20 um	Near IR, thermal IR	Vibration
Higher Energy	<1um	Visible, UV	Electronic

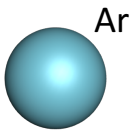
ROTATIONAL

Moment of Inertia

$$I = \sum_i r_i^2 \delta m_i$$

Molecule	*Structure*		*Permanent Electirc Dipole Moment?*
Oxygen		linear	No (has magnetic dipole moment)
Nitrogen		linear	No
Carbon Monoxide		linear	Yes
Carbon Dioxide		linear	No
Nitrous Oxide		linear	Yes
Water		asymmetric top	Yes
Ozone		asymmetric top	Yes
Methane		spherical top	No

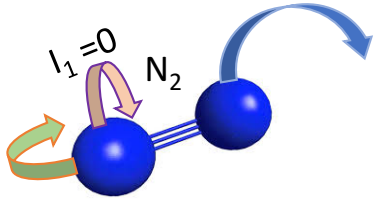
ROTATIONAL

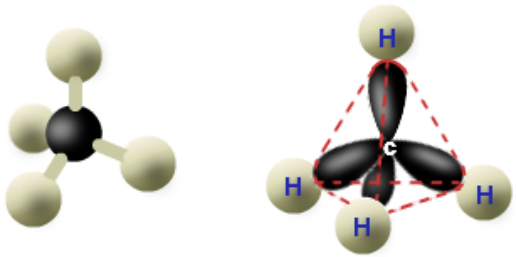


Simple Spectra

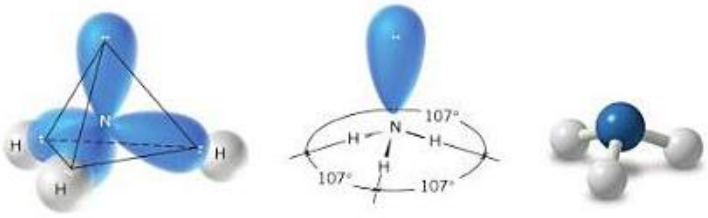
Most Complex Spectra

Description	Moments of Inertia	Examples
Monoatomic	$I_1 = I_2 = I_3 = 0$	Ar
Linear	$I_1 = 0$; $I_2 = I_3 > 0$	N_2, O_2, CO_2, N_2O
Spherical Top	$I_1 = I_2 = I_3 > 0$	CH_4
Symmetric Top	$I_1 \neq 0$; $I_2 = I_3 > 0$	NH_3, CH_3Cl, CF_3Cl
Asymmetric Top	$I_1 \neq I_2 \neq I_3$	H_2O, O_3

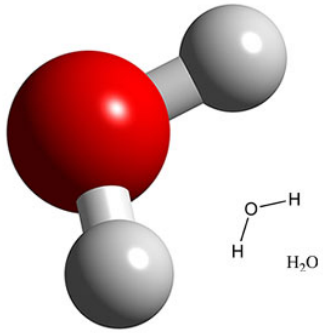




Tetrahedral geometry of methane



Molecular geometry of NH_3



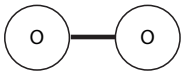
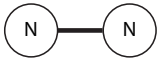
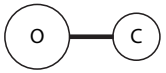
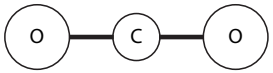
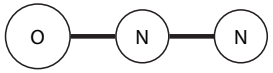
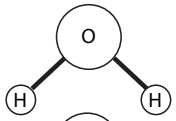
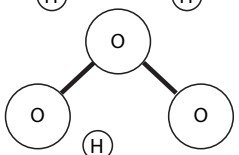
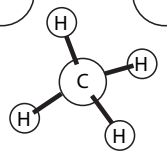
ROTATIONAL

Moment of Inertia

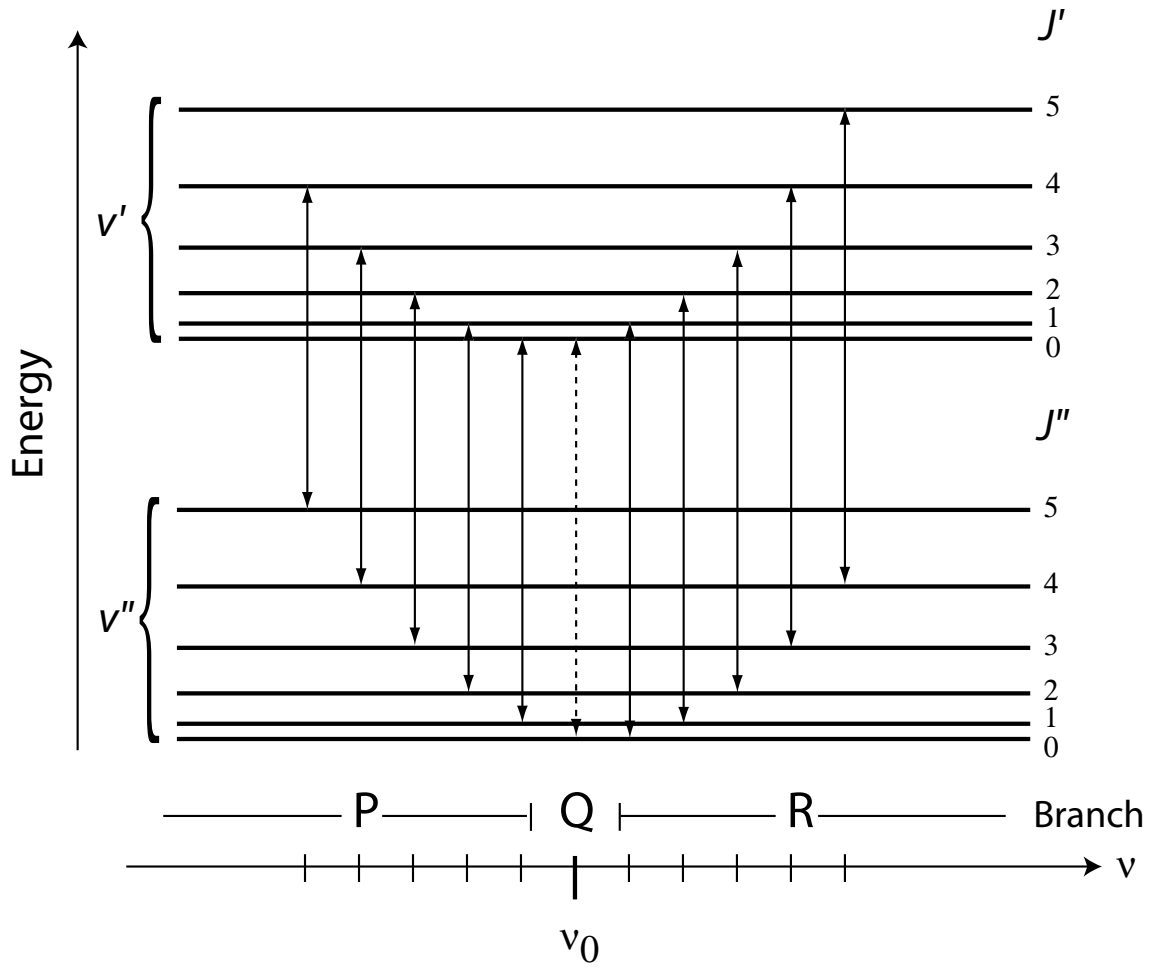
$$I = \sum_i r_i^2 \delta m_i$$

Angular Momentum of a rigid molecule is restricted to discreet values.

v=0,1,2,….
Rotational Quantum number

Molecule	*Structure*		*Permanent Electirc Dipole Moment?*
Oxygen		linear	No (has magnetic dipole moment)
Nitrogen		linear	No
Carbon Monoxide		linear	Yes
Carbon Dioxide		linear	No
Nitrous Oxide		linear	Yes
Water		asymmetric top	Yes
Ozone		asymmetric top	Yes
Methane		spherical top	No

Need to consider combination of rotational state and electronic state



ROTATIONAL

Moment of Inertia

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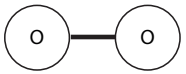
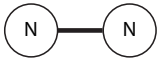
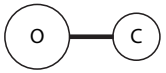
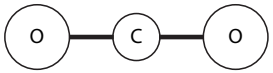
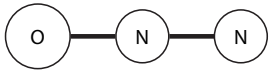
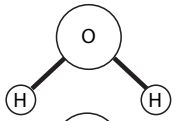
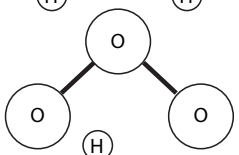
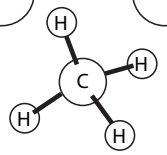
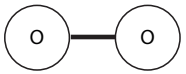
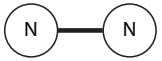
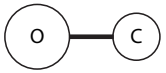
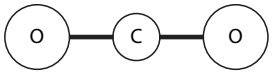
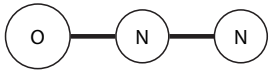
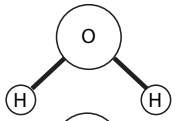
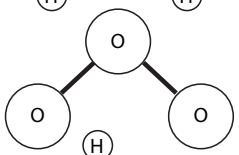
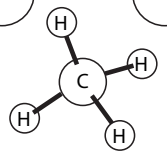
Molecule	*Structure*		*Permanent Electirc Dipole Moment?*
Oxygen		linear	No (has magnetic dipole moment)
Nitrogen		linear	No
Carbon Monoxide		linear	Yes
Carbon Dioxide		linear	No
Nitrous Oxide		linear	Yes
Water		asymmetric top	Yes
Ozone		asymmetric top	Yes
Methane		spherical top	No

Either an applied magnetic or electric field has the capacity to exert a torque on the molecule

ROTATIONAL

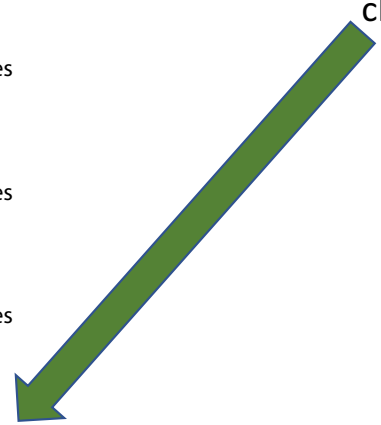
Moment of Inertia

$$I = \sum_i r_i^2 \delta m_i$$

Molecule	*Structure*		*Permanent Electirc Dipole Moment?*
Oxygen		linear	No (has magnetic dipole moment)
Nitrogen		linear	No
Carbon Monoxide		linear	Yes
Carbon Dioxide		linear	No
Nitrous Oxide		linear	Yes
Water		asymmetric top	Yes
Ozone		asymmetric top	Yes
Methane		spherical top	No

No rotation

No rotation
Without Vibration
changing geometry



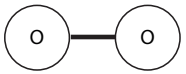
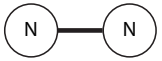
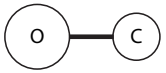
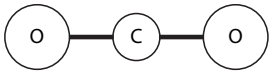
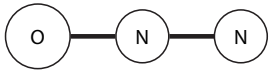
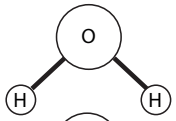
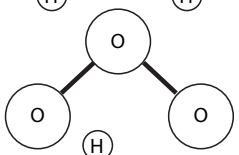
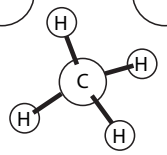
ROTATIONAL

Moment of Inertia

$$I = \sum_i r_i^2 \delta m_i$$

All other major molecules found in the atmosphere exhibit permanent electric dipole moment

Creating major rotational absorption bands

Molecule	*Structure*		*Permanent Electirc Dipole Moment?*
Oxygen		linear	No (has magnetic dipole moment)
Nitrogen		linear	No
Carbon Monoxide		linear	Yes
Carbon Dioxide		linear	No
Nitrous Oxide		linear	Yes
Water		asymmetric top	Yes
Ozone		asymmetric top	Yes
Methane		spherical top	No

No rotation

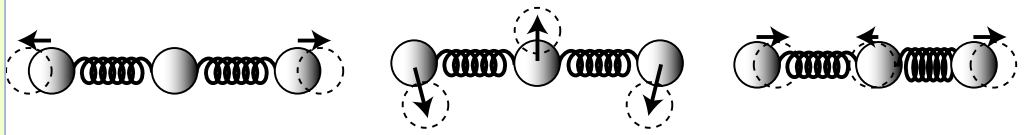
No rotation
Without Vibration
changing geometry

VIBRATIONAL

- Molecule behaves like a spring
- Vibrational transitions associated with larger energy than rotational transitions (shorter wavelengths)
- Vibrational and rotational transitions often occur simultaneously

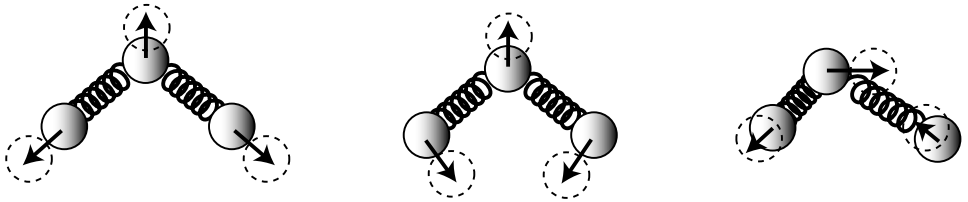
Diatomic (N_2, O_2, CO)

Linear triatomic (CO_2, N_2O)

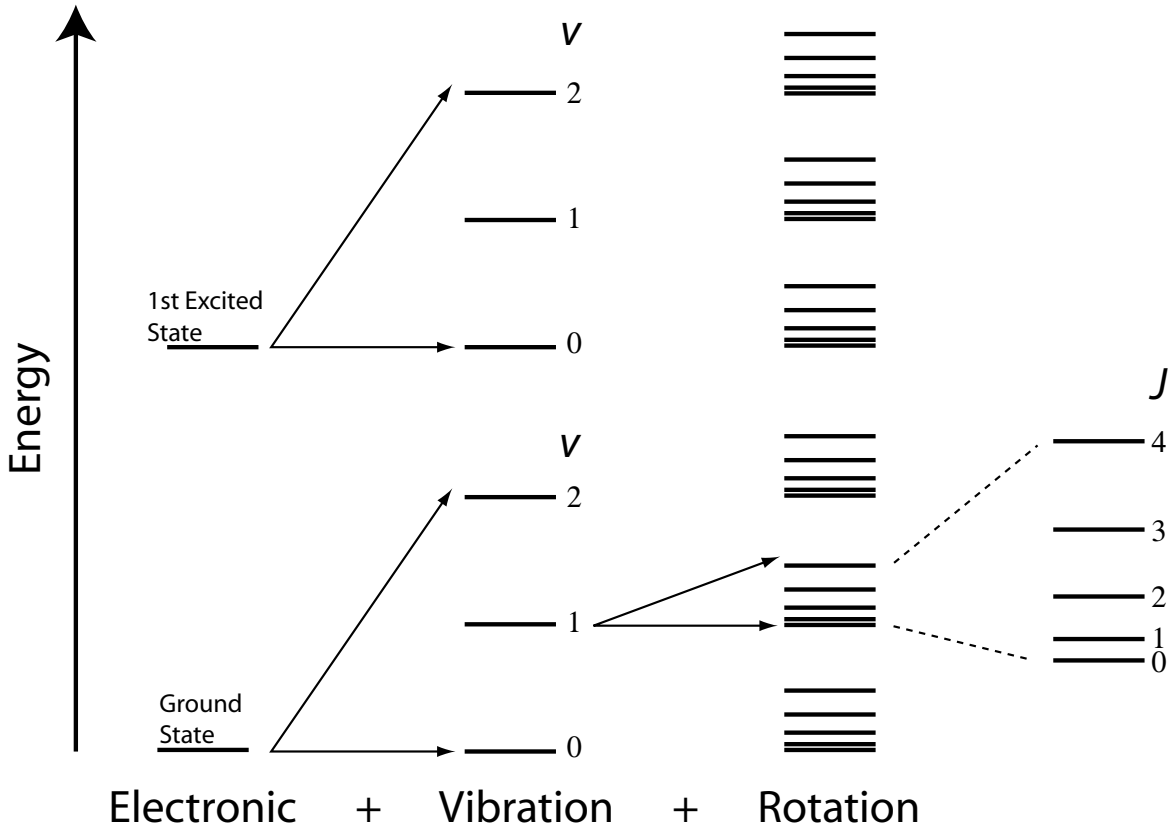


Symmetric stretch ν_1 | *Bending* ν_2 | *Asymmetric stretch* ν_3

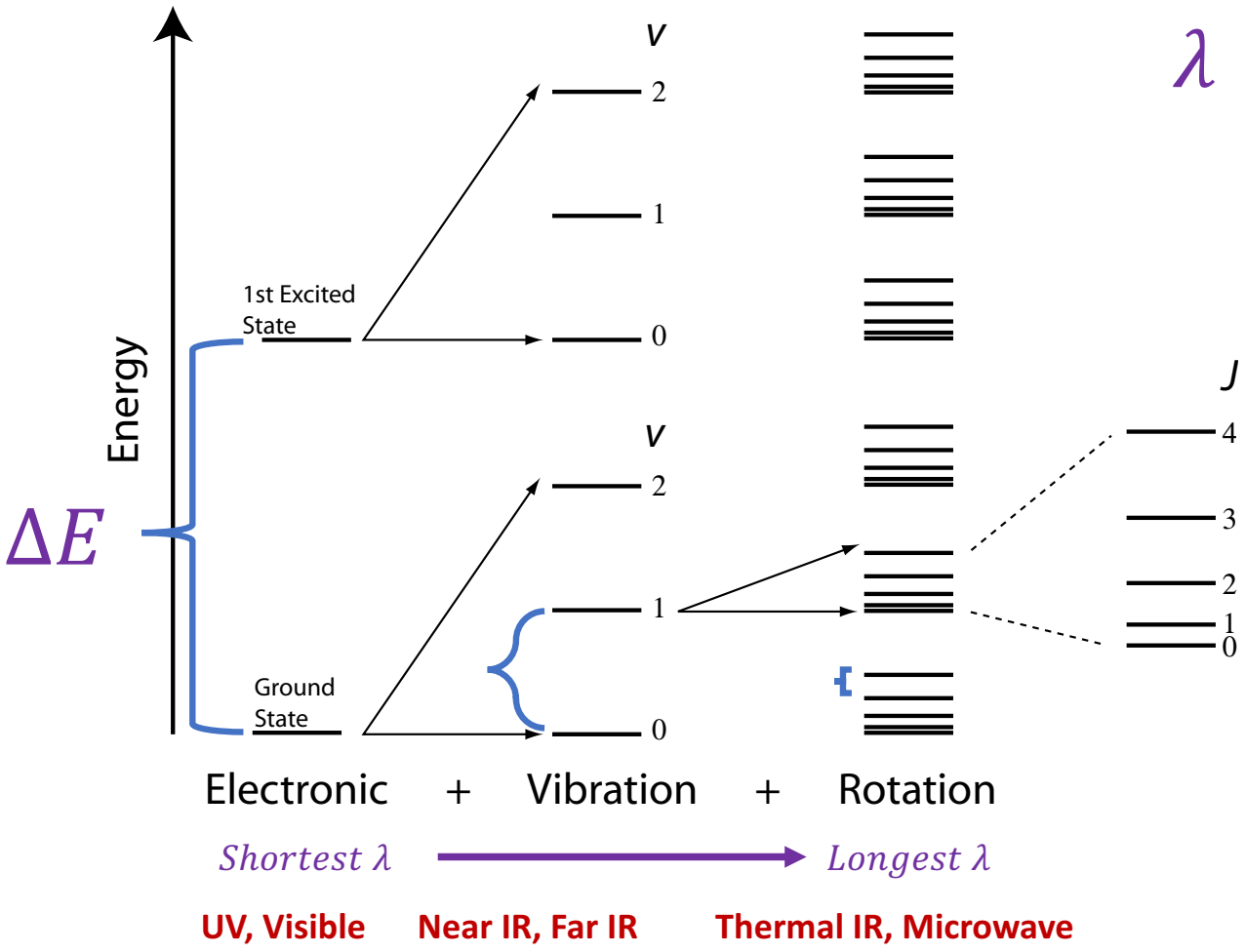
Nonlinear Triatomic (H_2O, O_3)

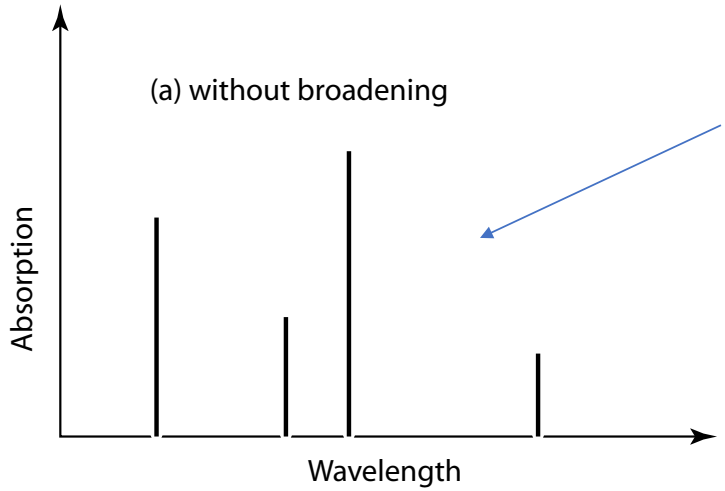


Symmetric stretch ν_1 | *Bending* ν_2 | *Asymmetric stretch* ν_3

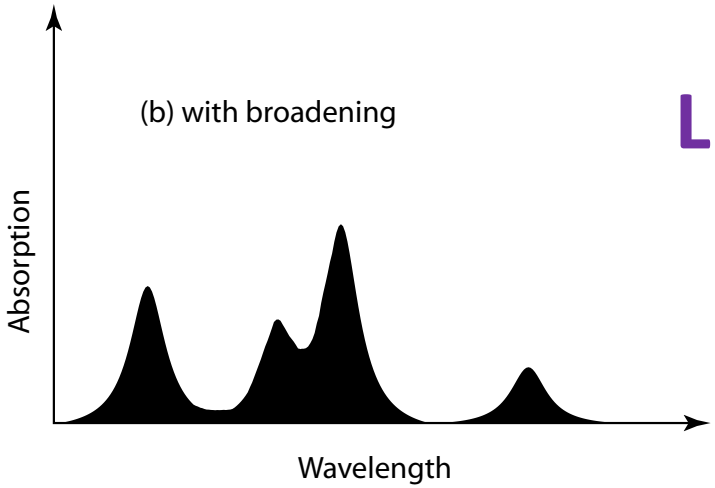

Energy
v
2
1
0
1st Excited State
v
2
1
0
Ground State
J
4
3
2
1
0
Electronic + Vibration + Rotation

$$\lambda = \frac{c}{\nu} = \frac{hc}{\Delta E}$$





NO Flux – Atmospheric Radiation Irrelevant



LINE SHAPE

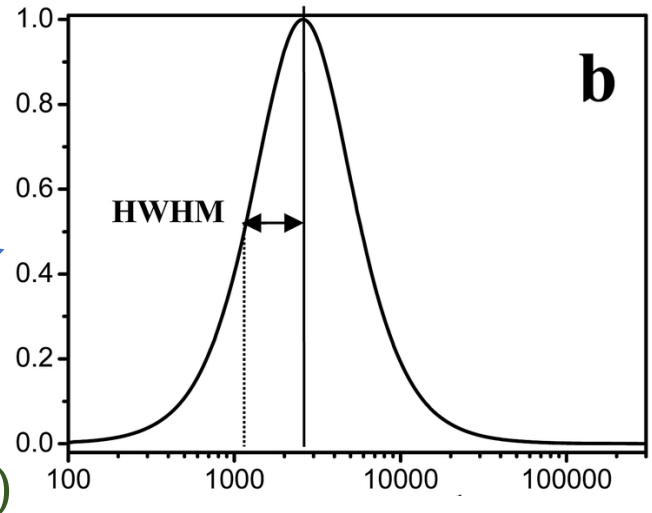
Describe a line shape

$$\boldsymbol{\sigma_v = Sf(\nu - \nu_o)}$$

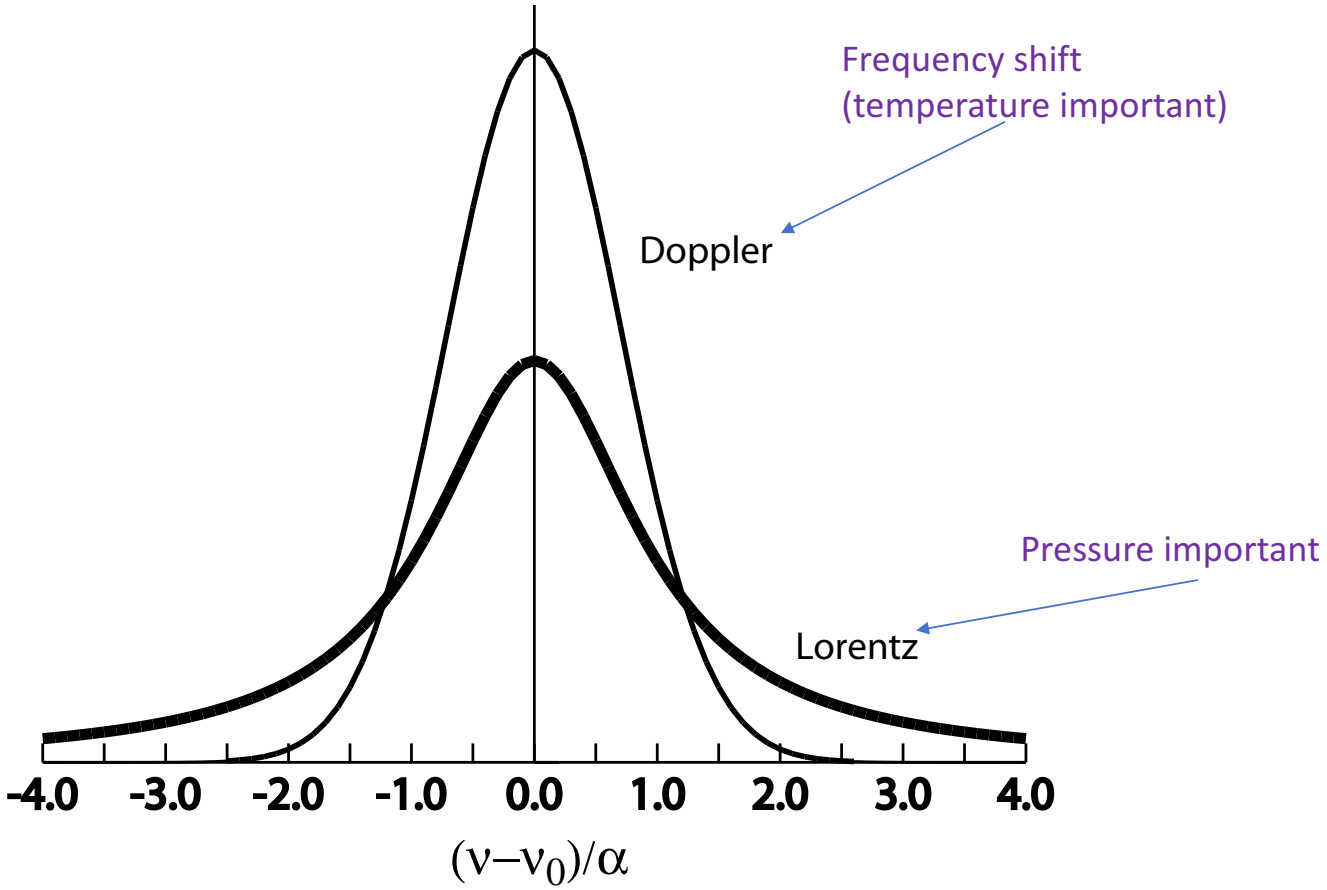
$\sigma_v = absorption\ cross\ section\ per\ molecule$

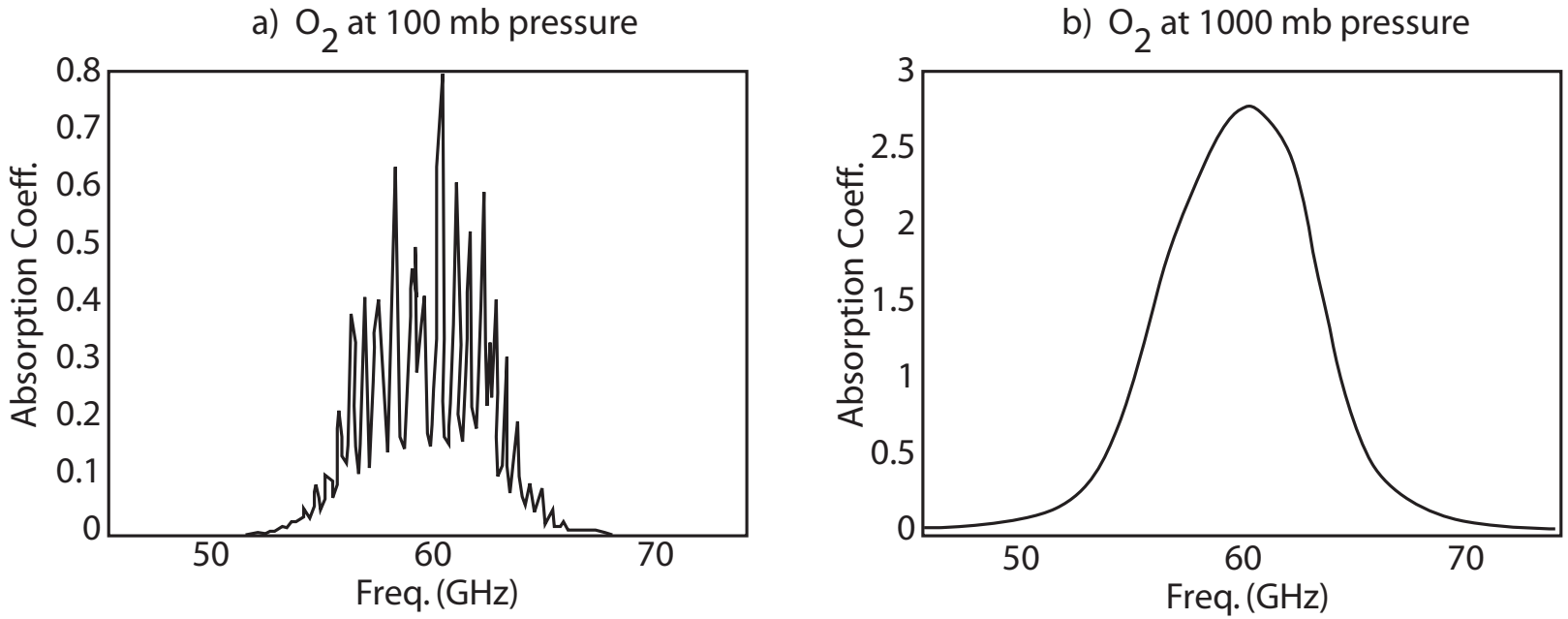
$S = line\ strength$

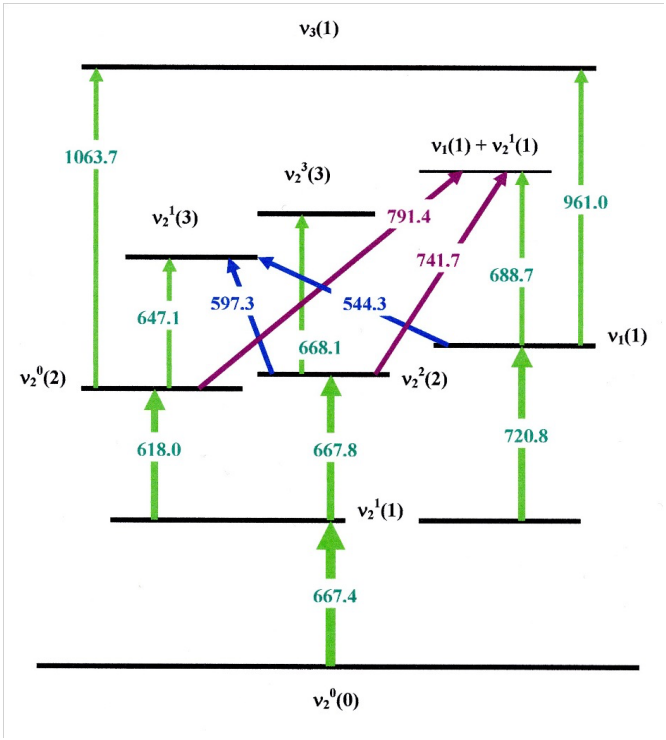
$f(\nu - \nu_o) = line\ shape\ function$



$\alpha_{1/2} = half\ width\ at\ half\ maximum\ (HWHM)$

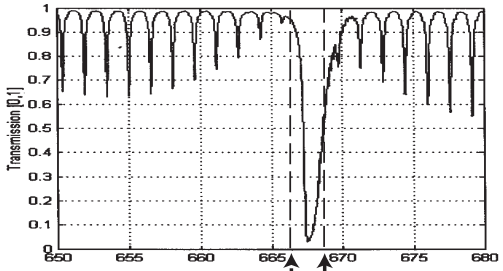

Frequency shift
(temperature important)
Doppler
Pressure important
Lorentz
-4.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
$(\nu-\nu_0)/\alpha$


a) O_2 at 100 mb pressure
Absorption Coeff.
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
60
70
Freq. (GHz)
b) O_2 at 1000 mb pressure
Absorption Coeff.
3
2.5
2
1.5
1
0.5
0
50
60
70
Freq. (GHz)

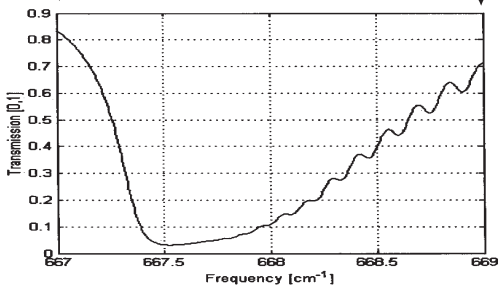


CO_2 Transmission in air over 1 m path

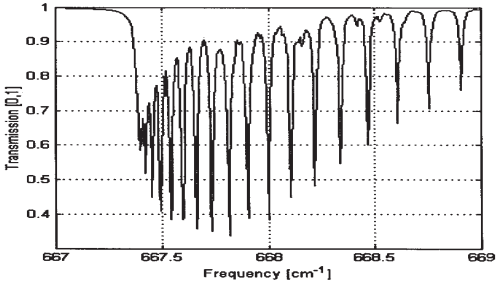
a) p = 1000 mb



b) p = 1000 mb



c) p = 100 mb



Problem 9.6
You need to use figure 6.4