

# Lecture 5: Spectroscopy and Photochemistry I

*Required Reading: FP Chapter 3*

*Suggested Reading: SP Chapter 3*

Atmospheric Chemistry  
CHEM-5151 / ATOC-5151  
Spring 2005  
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## Outline of Next Two Lectures

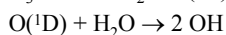
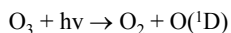
- Today
  - Importance of spectroscopy & photochemistry
  - Nature of light, EM spectrum
  - Molecular spectroscopy
- Thursday
  - The Sun as a radiation source
  - Light absorption
  - Atmospheric photochemistry

## Importance of Spectroscopy and Photochemistry I

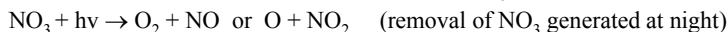
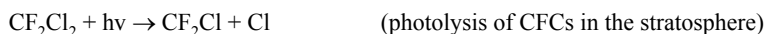
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- **Most chemical processes in the atmosphere are initiated by photons**

- Photolysis of O<sub>3</sub> generates OH – the most important atmospheric oxidizer:



- Solar photodissociation of many atmospheric molecules is often much faster than any other chemical reactions involving them:



etc.

## Importance of Spectroscopy and Photochemistry II

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- **Absorption of solar and earth radiation by atmospheric molecules directly influences the energy balance of the planet**

- Greenhouse effect (CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>O, CFCs)
- Stratospheric temperature inversion (O<sub>3</sub> photochemistry)

- **Spectroscopy of atmospheric molecules is used to detect them *in situ***

- OH is detected via its electronic transition at 310 nm
- NH<sub>3</sub> is detected via its fundamental vibrational transition at 1065 cm<sup>-1</sup>, etc.

## Solar Radiation: Initiator of Atmos. Reactions

### Average thermal energy of collisions:

$$\sim RT = 8.3 \text{ J mol}^{-1} \text{ K}^{-1} \times T$$
$$RT = 2.5 \text{ kJ mol}^{-1} @ 300 \text{ K}$$

### Energy of photons ( $E = h\nu$ ):

$$300 \text{ nm photon} = 380 \text{ kJ mol}^{-1}$$
$$600 \text{ nm photon} = 190 \text{ kJ mol}^{-1}$$

### Typical bond strengths:

$$D_0(\text{O}_2) = 495 \text{ kJ mol}^{-1}$$
$$D_0(\text{Cl}_2) = 243 \text{ kJ mol}^{-1}$$
$$\text{C-H, O-H, C-O} \sim 400 \text{ kJ mol}^{-1}$$

*Atmospheric chemistry on Earth is driven by photolysis, not by thermal excitation!!!*

From S. Nidkorodov

## What is light?

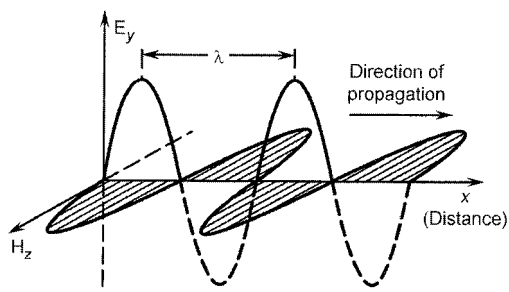


FIGURE 3.10 The instantaneous electric ( $E_y$ ) and magnetic ( $H_z$ ) field strength vectors of a plane-polarized light wave as a function of position along the axis of propagation ( $x$ ) (from Calvert and Pitts, 1966).

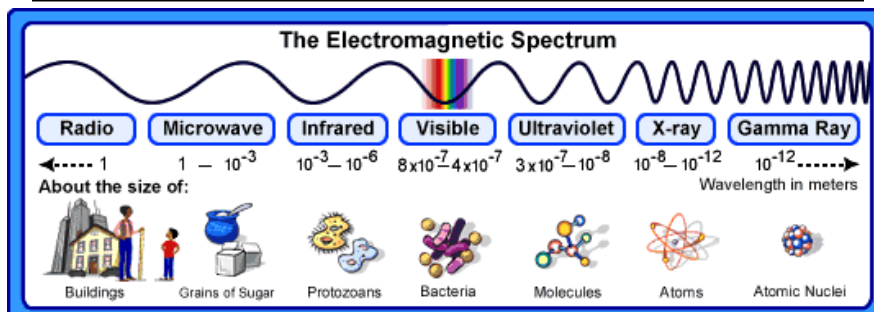
From F-P&P

*Discuss in class: at a fundamental physical level, why are molecules capable of absorbing light?*

### Dual nature

- Photon: as particle
  - Energy but no mass
- As wave: electric and magnetic fields oscillating in space and time
  - Wavelength, frequency
  - $c \sim 3 \times 10^9 \text{ m/s}$

# The Electromagnetic Spectrum



- Units used for photon energies and wavelengths:
  - 1 eV = 8065.54 cm<sup>-1</sup> = 96.4853 kJ/mol = 23.0605 kcal/mol = 11604.4 K
  - 1 Å = 0.1 nm = 10<sup>-10</sup> m; micron = 10<sup>-6</sup> m = 1000 nm
- Solve in class: Calculate the energy, frequency, and wavenumber of a green photon ( $\lambda = 530$  nm).

$$\lambda = \frac{c}{\nu}$$

$$E = h\nu$$

$$\bar{\nu} = \frac{1}{\lambda}$$

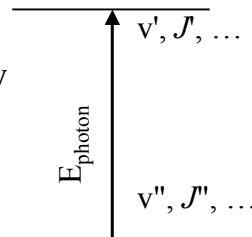
(wavenumber)

## Types of radiation important in lower atmosphere

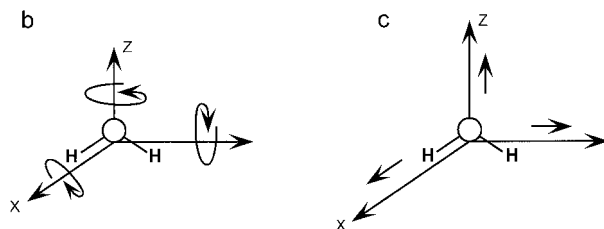
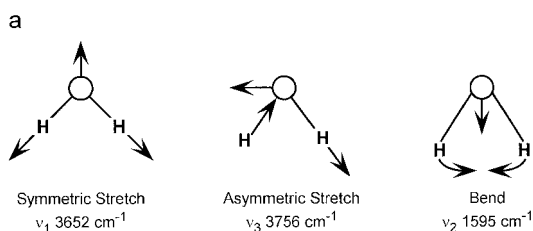
- Ultraviolet and visible radiation ( $\lambda = 100$ -800 nm)
  - Excites bonding electrons in molecules
  - **Capable of breaking bonds in molecules** ( $\Rightarrow$  photodissociation)
  - Ultraviolet photons ( $\lambda = 100$ -300 nm) have most energy, can break more and stronger bonds. We will pay special attention to them.
- Infrared radiation ( $\lambda = 0.8$  - 300  $\mu$ m)
  - Excites vibrational motions in molecules
  - With a very few exceptions, infrared radiation is not energetic enough to break molecules or initiate photochemical processes
- Microwave radiation ( $\lambda = 0.5$  - 300 mm)
  - Excites rotational motions in molecules

# Fundamentals of Spectroscopy

- Molecules have energy in translation, vibration, rotation, and electronic state
  - Translation (= T) cannot be changed directly with light
  - We will focus on the other 3 energy types
- Molecule can absorb radiation efficiently if:
  - The photon energy matches the energy spacing between molecule's quantum levels
  - Optical transition between these quantum levels is allowed by "selection rules"
  - "Forbidden" transitions can occur but are weaker



# Vibrational Energy & Transitions



- Bonds can be viewed as "springs"
- Energy levels are quantized,
  - $E_v = h\nu_{vib}(v+1/2)$
  - $\nu_{vib}$  is constant dependent on molecule
  - $v = 0, 1, 2, \dots$  is vibrational quantum number

FIGURE 3.1 (a) Internal vibrations of the bonds in the water molecule, (b) rotational motion of water, and (c) translation of the water molecule.

From F-P&P

## Vibrational Energy Levels

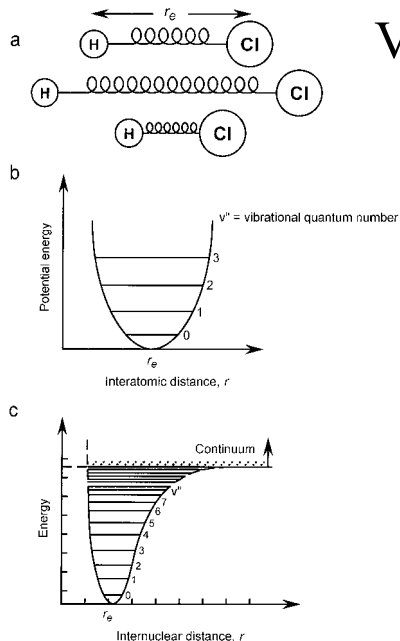


FIGURE 3.2 (a) Vibration of diatomic molecule, HCl, (b) potential energy of an ideal harmonic oscillator, and (c) an anharmonic oscillator described by the Morse function.

- Ideally: Harmonic Oscillator
  - Restoration force of “spring” follows Hooke’s law:  $F = k \Delta x$
  - $E_v = h\nu_{vib}(v+1/2)$ ,  $v = 0, 1, 2, \dots$
  - Energy levels are equally spaced
- Really: Anharmonic oscillator
  - Restoration force rises sharply at small  $r$ , bond breaks at large  $r$

$$E_{vib} = h\nu\left(v + \frac{1}{2}\right) - h\nu x_e\left(v + \frac{1}{2}\right)^2 + h\nu y_e\left(v + \frac{1}{2}\right)^3 + \dots$$

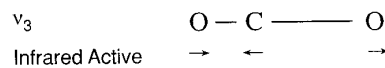
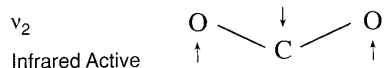
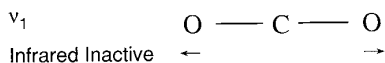
- Vibrational quantum levels are more closely spaced as  $v$  increases

From F-P&P

## Vibrational Selection Rules

- For ideal harmonic oscillator
  - $\Delta v = \pm 1$
- For anharmonic oscillator
  - $\Delta v = \pm 2, \pm 3$  weaker “overtone” transitions can occur
- At room T most molecules at  $v = 0$ 
  - Energy spacing of levels is large ( $\sim 1000 \text{ cm}^{-1}$ )
  - $v' = 0 \rightarrow v' = 1$  is by far strongest
- For purely vibrational transition
  - Absorption of light can occur if dipole moment changes during vibration. E.g. HCl, CO, NO
  - Homonuclear diatomics, e.g.  $\text{O}_2$ ,  $\text{N}_2$  don’t have v.t.

## Infrared Active and Inactive Modes



- Only vibrational modes that change the dipole moment can interact with light and lead to absorption
- CO<sub>2</sub> is infrared active, but not all of its modes are

**Figure 3.2.** Illustration of the infrared-active and -inactive vibrational modes of CO<sub>2</sub>. Modes  $\nu_2$  and  $\nu_3$  lead to a change in the dipole moment, and are thus infrared active.

## Rotational Energy and Transitions

- If molecule has permanent dipole
  - Rotation in space produces oscillating electric field
  - Can interact with light's fields and result in absorption
  - *Only heteronuclear molecules*

- Rigid rotor
  - No simultaneous vibration
  - Allowed energy levels:

$$E_{rot} = BJ(J+1) \text{ cm}^{-1}$$

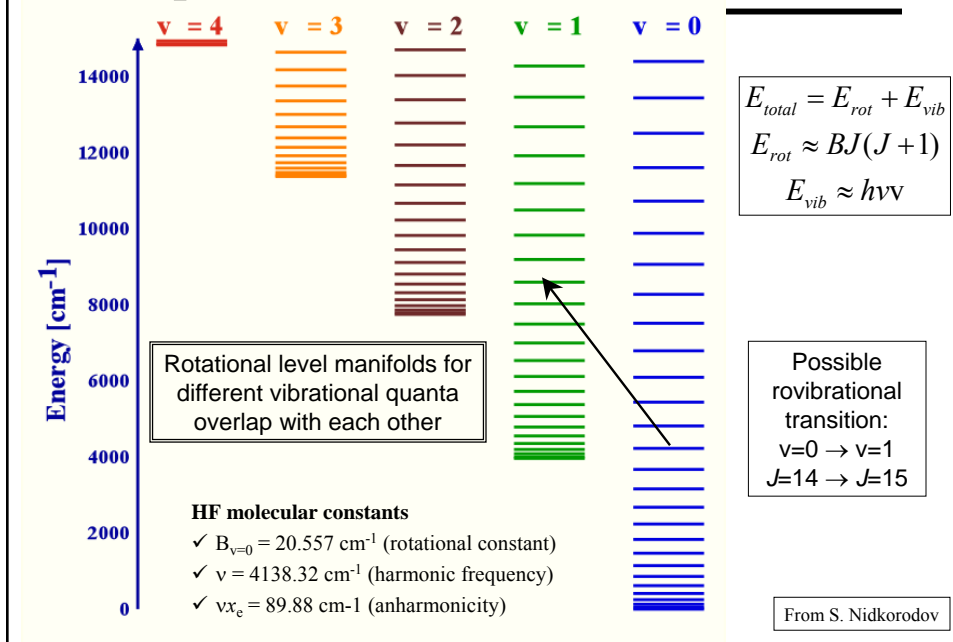
$$B = \frac{h^2}{8\pi^2 I} \text{ where } I = \frac{m_1 m_2}{m_1 + m_2} R^2$$

- Nonrigid rotor

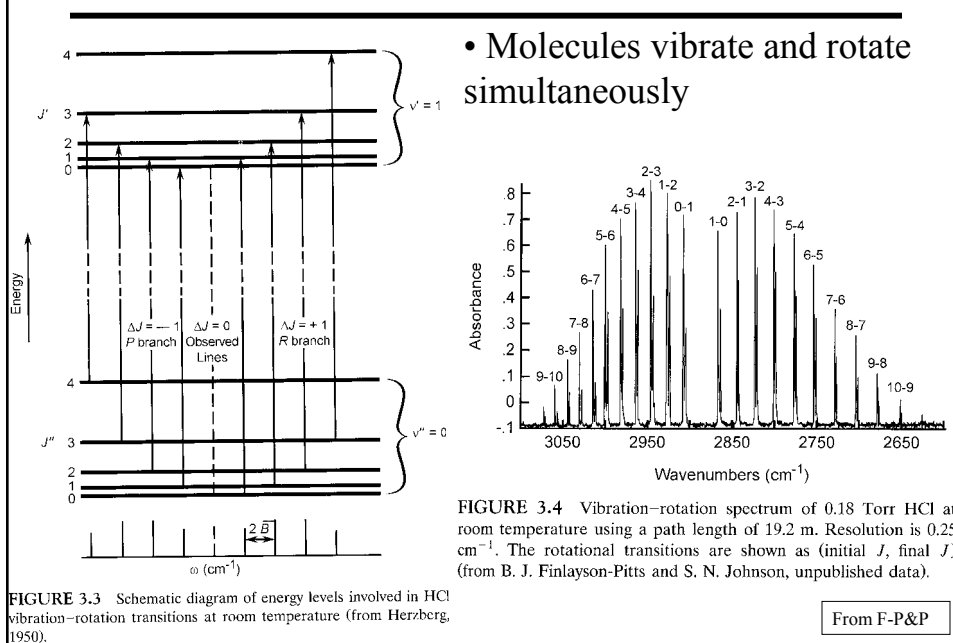
$$E_{rot} = BJ(J+1) - DJ^2(J+1)^2 + \dots$$

- Spacing increases with  $J$
- Spacing between levels small, many levels are populated

## Example: Ground Electronic State of HF



## Vibration-rotation of HCl





# Electronic Energy and Transitions

- Several additional quantum numbers
  - $\Lambda$ : related to electronic angular momentum
  - $S$ : spin number
    - Multiplicity =  $(2S + 1)$
    - Mult = 1, 2, 3 are referred to as singlet, doublet, triplet
    - Most stable molecules have singlet ground states
    - $O_2$  has triplet ground state, important exception

From F-P&P

- $\Omega = |\Lambda + \Sigma|$ 
  - $\Sigma = +S, S-1, \dots, -S$
- “g” or “u” states
- “+” or “-” states of  $\Sigma$

- More complex selection rules involving these numbers:

TABLE 3.1 Allowed<sup>a</sup> Electronic Transitions of Diatomic Molecules Having Light Nuclei<sup>b</sup>

Homonuclear diatomic (equal nuclear charge)	Heteronuclear diatomic (unequal nuclear charge)
$\Sigma_g^+ \leftrightarrow \Sigma_u^-$	$\Sigma^+ \leftrightarrow \Sigma^-$
$\Sigma_g^- \leftrightarrow \Sigma_u^+$	$\Sigma^- \leftrightarrow \Sigma^+$
$\Pi_g \leftrightarrow \Sigma_u^+, \Pi_u \leftrightarrow \Sigma_g^-$	$\Pi \leftrightarrow \Sigma^+$
$\Pi_g \leftrightarrow \Sigma_u^-, \Pi_u \leftrightarrow \Sigma_g^+$	$\Pi \leftrightarrow \Sigma^-$
$\Pi_g \leftrightarrow \Pi_u$	$\Pi \leftrightarrow \Pi$
$\Pi_g \leftrightarrow \Delta_u, \Pi_u \leftrightarrow \Delta_g$	$\Pi \leftrightarrow \Delta$
$\Delta_g \leftrightarrow \Delta_u$	$\Delta \leftrightarrow \Delta$

<sup>a</sup> Presuming that the rule  $\Delta S = 0$  is obeyed.

<sup>b</sup> Source: Herzberg (1950), p. 243.

# Electronic Transitions (ETs)

- Molecules can undergo an ET upon absorption of an appropriate photon
  - Simultaneous vibrational and rotational transitions
  - No restriction on  $\Delta v$ , many vib. trans. can occur
  - $\Delta J = -1, 0, +1$ 
    - P, Q, and R branches
- Frank-Condon principle
  - Time for ET so short ( $10^{-15}$  s) that internuclear distance cannot change
  - “vertical” transitions

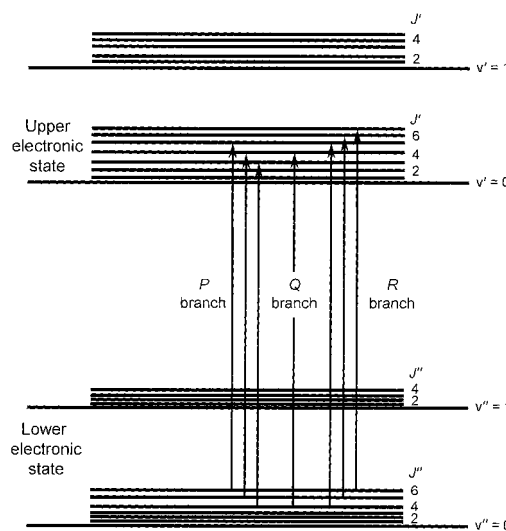


FIGURE 3.5 Schematic of some possible rotational and vibrational transitions involved during an electronic transition of a diatomic molecule from the ground electronic state.

From F-P&P

## Potential Energy Curves for an ET

- At room T,  $v''=0$
- Prob of transition proportional to product of vib. wavefunctions
  - Transition to  $v'=4$  in upper electronic state most intense

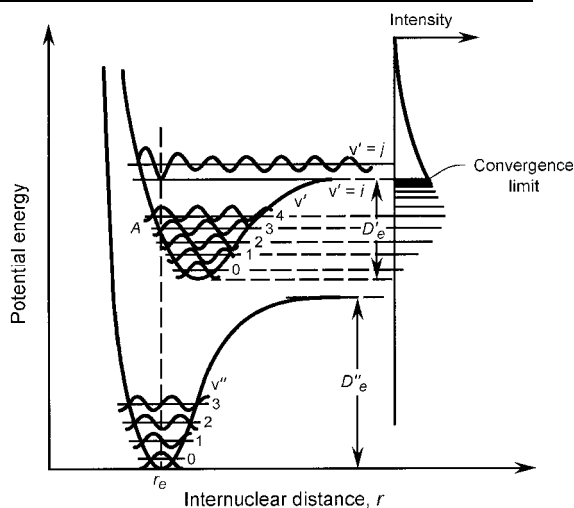


FIGURE 3.6 Potential energy curves for the ground state and an electronically excited state of a hypothetical diatomic molecule. Right-hand side shows relative intensities expected for absorption bands (from Calvert and Pitts, 1966).

From F-P&P

## Repulsive States

- No minima in PE vs  $r$  curves
- Dissociation occurs immediately after absorption of light

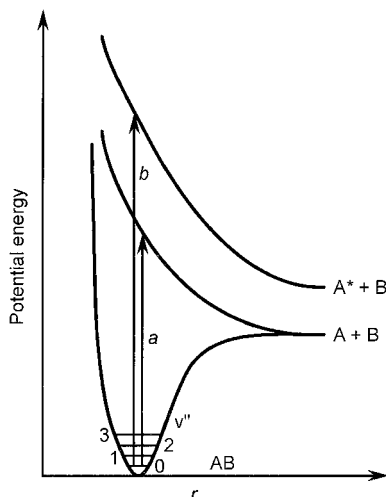
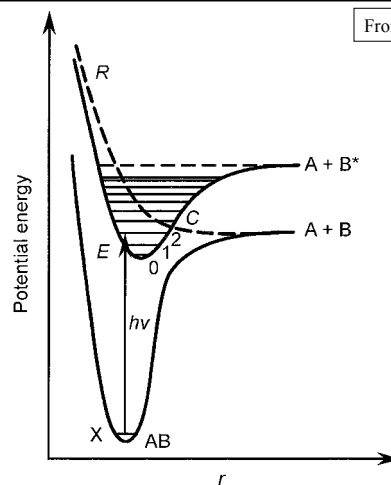


FIGURE 3.7 Potential energy curves for a hypothetical diatomic molecule showing electronic transitions to two repulsive excited states having no minima.  $A^*$  is an electronically excited atom.

From F-P&P

## More complex case & Predissociation

- Some repulsive and some non-repulsive upper elec. states
- Example
  - Trans. to R causes immediate dissociation
  - Trans. to E can lead to dissociation if cross over to state R occurs
    - “Predissociation”
  - If high enough energy, trans. to E can yield  $A + B^*$



From F-P&P

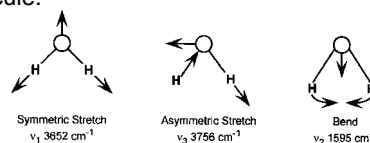
FIGURE 3.8 Potential energy curves for the ground state and two electronically excited states in a hypothetical diatomic molecule. Predissociation may occur when the molecule is excited into higher vibrational levels of the state E and crosses over to repulsive state R at the point C (from Okabe, 1978).

## Polyatomic Molecules

From S. Nidkorodov

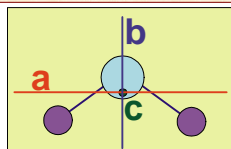
1. Number of vibrations increases to  $s = 3N - 6$  ( $s = 3N - 5$  for linear molecules), where  $N$  is the number of atoms in the molecule:

$$\begin{array}{lll} \text{H}_2\text{O}: & N = 3 & \Rightarrow s = 3 \\ \text{C}_6\text{H}_6: & N = 12 & \Rightarrow s = 30 \\ \text{C}_{60}: & N = 60 & \Rightarrow s = 174 \end{array}$$

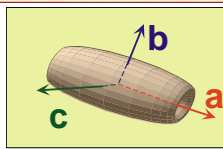


2. Three independent axes of rotation, each characterized by its own rotational constant ( $A$ ,  $B$ ,  $C$ ):

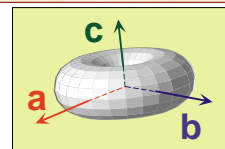
**Asymmetric tops  $A \neq B \neq C$**   
**H<sub>2</sub>O molecule, meat grinder**



**Prolate symmetric tops  $A < B = C$**   
**CH<sub>3</sub>F molecule; a pencil**



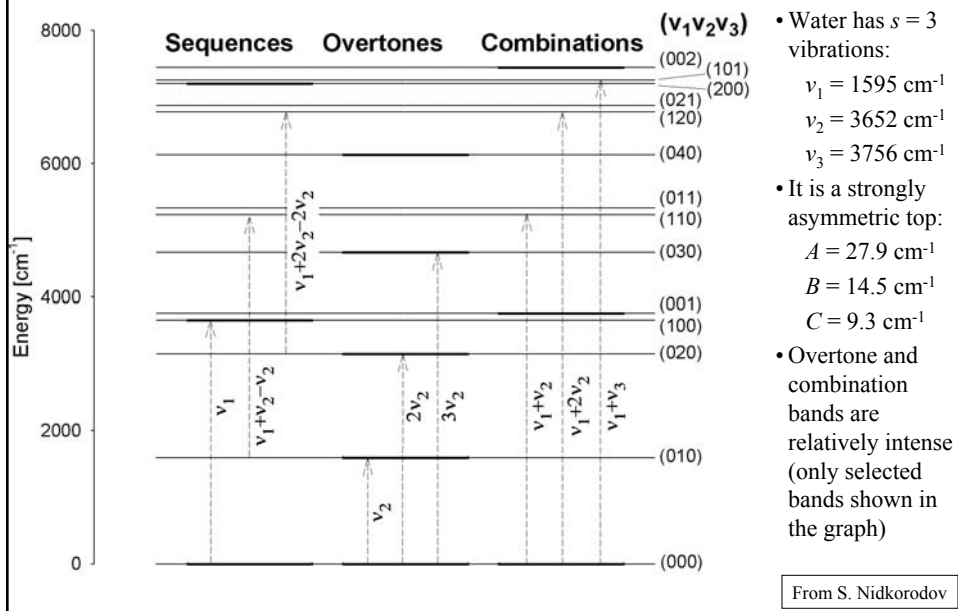
**Oblate symmetric tops  $A = B < C$**   
**CH<sub>3</sub> radical, planet Earth**



3. Complexity of the absorption spectrum increases very quickly with  $N$ . New types of bands become possible:

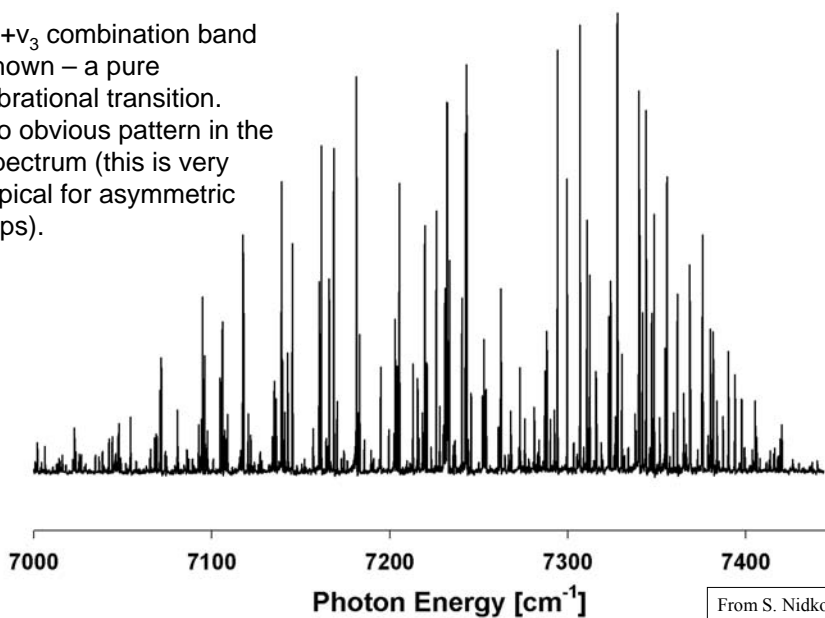
- ✓ **Sequence bands**: one vibration excited while maintaining excitation in another vibration (allowed)
- ✓ **Combination bands**: two different vibrations excited simultaneously (forbidden in harmonic approximation)
- ✓ **Overtone bands** are also possible, just like for diatomic molecules (forbidden in harmonic approximation)

## Example: Vibrational Spectrum of H<sub>2</sub>O



## Sample Near-IR Spectrum of H<sub>2</sub>O

- $v_1+v_3$  combination band shown – a pure vibrational transition.
- No obvious pattern in the spectrum (this is very typical for asymmetric tops).



## Pathways for Loss of e<sup>-</sup> Excitation

- Photophysical processes
  - Lead to emission of radiation
  - Energy converted to heat
  - Read details in book
- Photochemical processes
  - Dissociation, ionization, reaction, isomerization

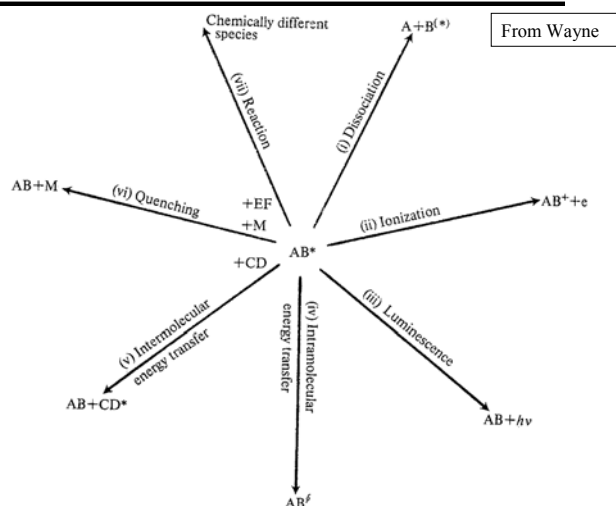


Fig. 3.1. Pathways for loss of electronic excitation that are of importance in atmospheric chemistry. The use of the symbols \* and § illustrates the presence of electronic excitation: the products of any of the processes may be excited. With the exception of pathways (i) and (iv), excited atoms can participate as well as excited molecules.

## Photochemical processes

- Can produce new chemical species
- Photodissociation
  - most important by far
  - E.g. sole source of O<sub>3</sub> in troposphere:  

$$\text{NO}_2(\text{X}^2\text{A}_1) + h\nu (290 < \lambda < 430 \text{ nm}) \rightarrow \text{NO}(\text{X}^2\text{P}) + \text{O}(\text{P})$$
- Others: intramolecular rearrangements, photoisomerization, photodimerization, H-atom abstraction, and photosensitized reactions
- Reminder: photochemistry *drives* the chemistry of the atmosphere

## Quantum Yields ( $\phi$ )

- Relative efficiency of various photophysical and photochemical processes:

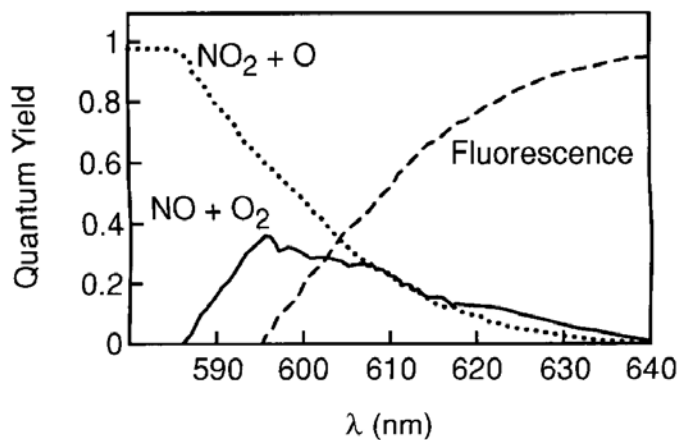
$$\phi_i = \frac{\text{Number of excited molecules proceeding by process } i}{\text{Total number of photons absorbed}}$$

- E.g.:
  - $\text{NO}_3 + h\nu \rightarrow \text{NO}_3^*$  (3)
  - $\text{NO}_3^* \rightarrow \text{NO}_2 + \text{O}$  (4a)
  - $\quad \quad \rightarrow \text{NO} + \text{O}_2$  (4b)
  - $\quad \quad \rightarrow \text{NO}_3 + h\nu$  (4c)

$$\phi_{4a} = \frac{\text{Number of NO}_2 \text{ molecules formed}}{\text{Total number of photons absorbed}} \quad \text{and so on}$$

- $\phi_i$  Are wavelength dependent, all important at different  $\lambda$

## Quantum Yields II



**FIGURE 4.18** Quantum yields for  $\text{NO}_3$  photolysis: dotted line,  $\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}$ ; solid line,  $\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$ ; dashed line, fluorescence quantum yields (adapted from Johnston *et al.*, 1996).