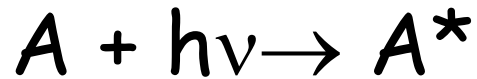# Lecture 6 – Photolysis

## CHEM/ATOC 5151

# What is photolysis?

- Unimolecular decomposition process initiated by absorption of a photon

- A + h$\nu \rightarrow$ B + C

- Treat like any other reaction:
  - Rate = J[A]

# Components of "J"

- Absorption spectrum of molecule
- Available light to interact with molecule
- Quantum yield of reactant $\rightarrow$ products
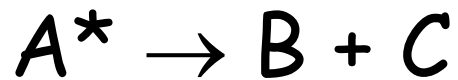
  $\Phi$ = # molecules dissociated/# photons absorbed

# Photon interactions with molecules

$A + h\nu \rightarrow A^*$        excitation

$A^* \rightarrow A + h\nu$        fluorescence

$A^* \rightarrow B + C$        photodissociation

$A^* \rightarrow A^+ + e^-$        photoionization
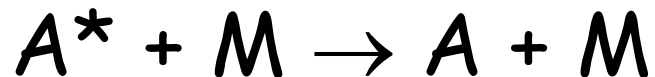
$A^* + M \rightarrow A + M$        quenching

# Electromagnetic Spectrum
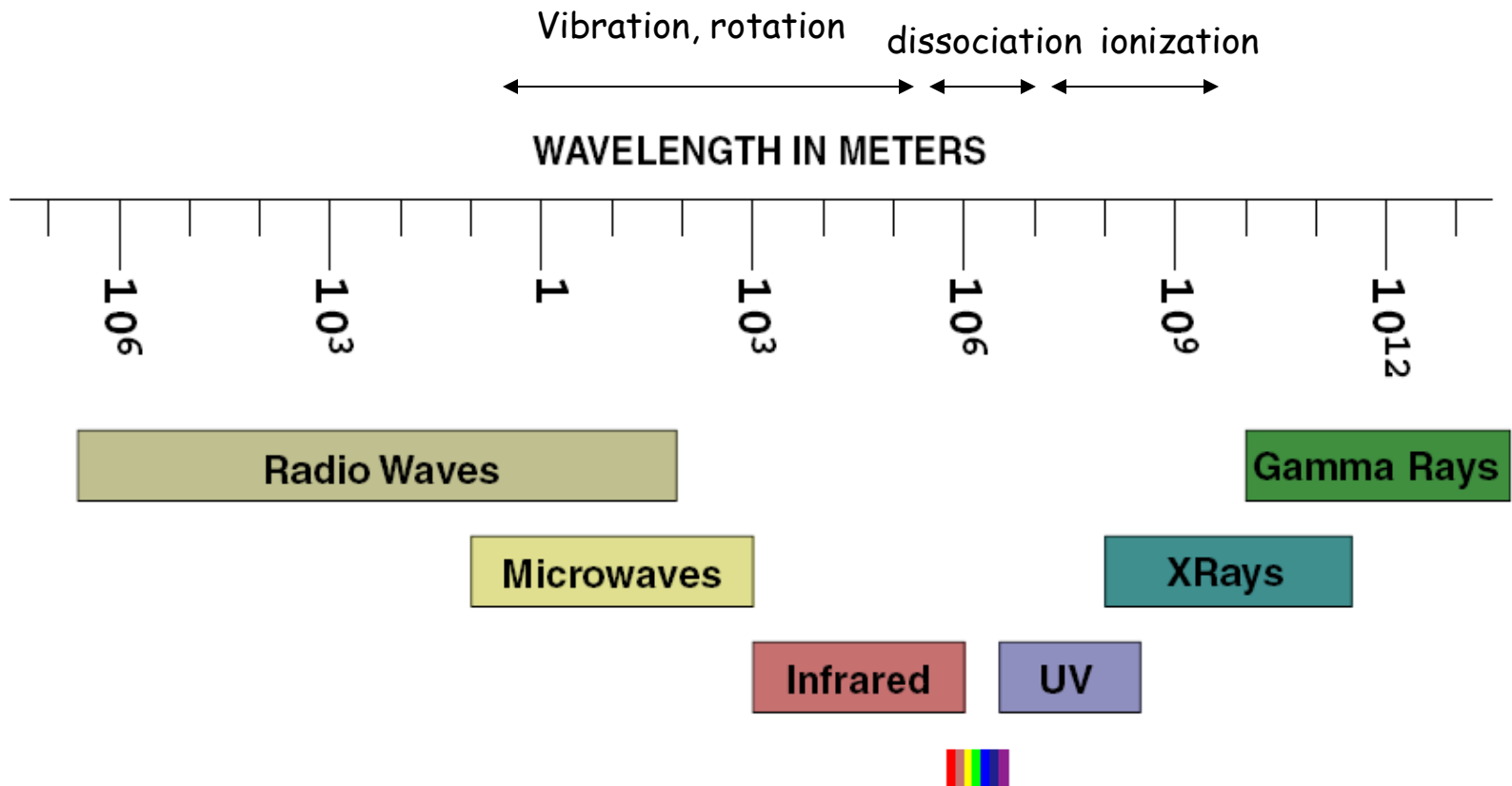
# What wavelengths matter?

- Amount of energy needed to break a bond

Example: $O_2 + h\nu \rightarrow O + O$
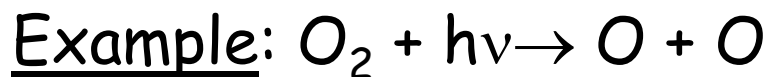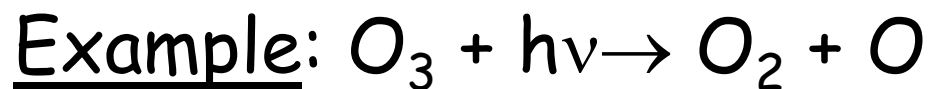
$\Delta H_{rxn} = 119.14$ kcal mol$^{-1}$ = $8.28 \times 10^{-19}$ J molec$^{-1}$

Recall that $E = h\nu = hc/\lambda$

So, $\lambda = hc/E = \dfrac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^{10} \text{ cm s}^{-1})}{8.28 \times 10^{-19} \text{ J}}$

$\lambda = 2.4 \times 10^{-7}$ m = 240 nm

# What wavelengths matter?

## Example: $O_3 + h\nu \rightarrow O_2 + O$

$\Delta H_{rxn}$ = 25.5 kcal mol$^{-1}$ = 1.77 x 10 $^{-19}$ J molec$^{-1}$

$\lambda$ = 1123 nm  (near infrared)

Thermodynamics provides a "first cut" to determine products for a given wavelength, but really need to look at the spectroscopic parameters to determine if photolysis will occur.

# The "rules"

Most photolytic processes are based on an electronic transition

- $\Delta E$ between the electronic states determines the photon energy required
- Intensity of the transition depends on the details of the two states – electronic transition moment
- Selection rules determine whether a transition is allowed.

# Term Symbols - Atoms

## Shorthand to describe electronic state

$^{Y}\mathbf{X}$ ← orbital angular momentum (L)

Spin angular momentum
(2s + 1), where each unpaired electron gives ½

| L=0 | S |
|-----|---|
| L=1 | P |
| L=2 | D |

# Term Symbols

<u>Example</u> – the oxygen atom

O has 8 electrons: $1s^2 2s^2 2p^4$

Refer to drawings on board…

Ground state oxygen is O($^3$P), whereas the most common excited state is O($^1$D). They differ in energy by almost 44 kcal mol$^{-1}$.

# Term Symbols - Molecules

$$^{(2s+1)}\Lambda^{ref}_{sym}$$

$\Lambda$ is orbital angular momentum ($\Sigma$, $\Pi$, $\Delta$, ...)

*ref* is reflection through the plane of the atoms

  (+, even, - odd)

*sym* is the symmetry of the wavefunction reflected through the center of the molecule
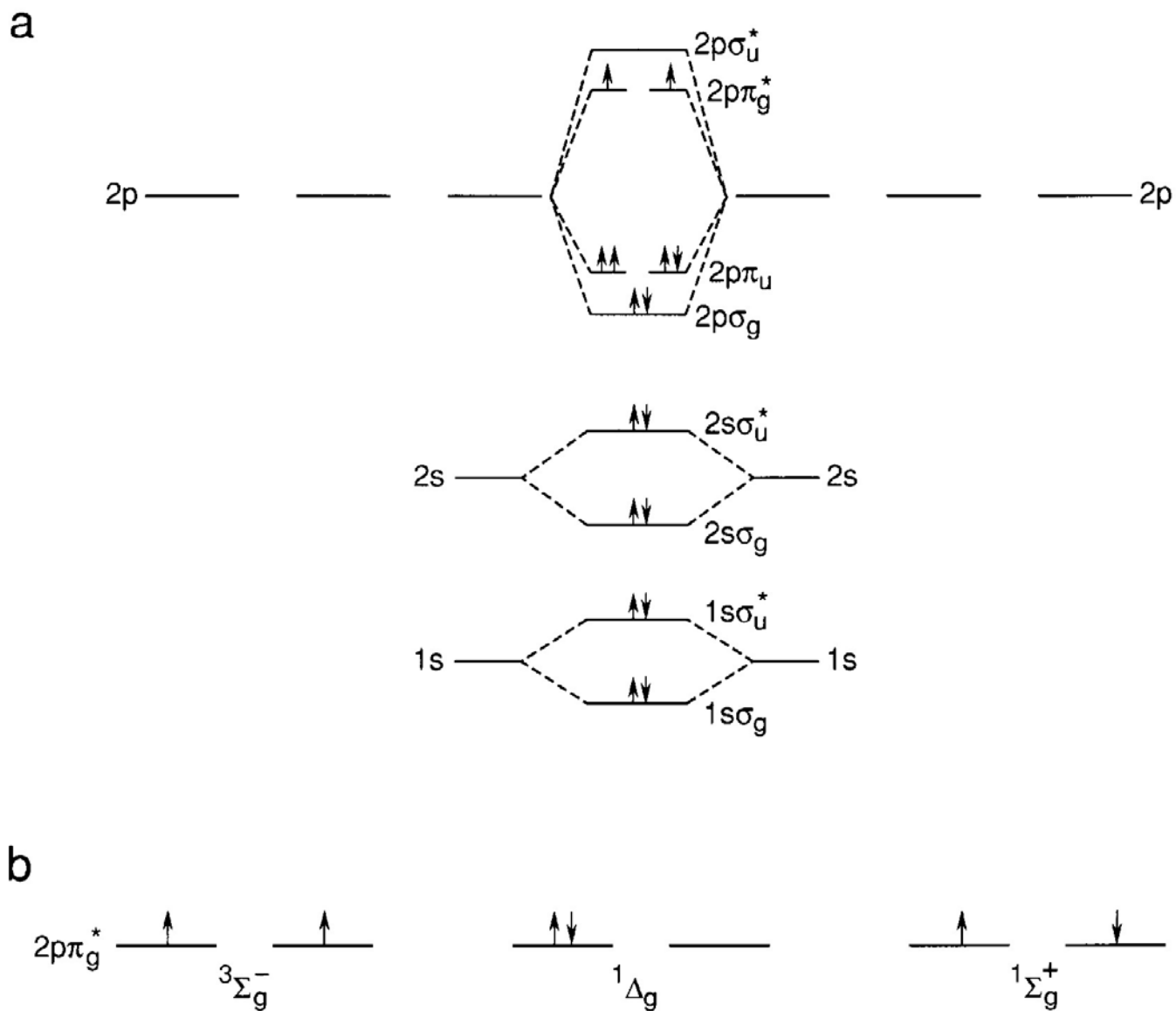
  (g, even; u, odd)

# Term Symbols - Molecules

<u>Example</u> – the oxygen molecule

Ground state oxygen (referred to as $X$) is $O_2(^3\Sigma_g^-)$, whereas the most common excited state ($a$) is $O_2$ ($^1\Delta_g$). They differ in energy by almost 22.5 kcal mol$^{-1}$.

The second excited state ($b$) is $O_2$ ($^1\Sigma_g^+$), which is 37.5 kcal mol$^{-1}$ above the ground state

**FIGURE 4.5** (a) Molecular orbital diagram of ground $X^3\Sigma_g^-$ state of $O_2$. (b) Comparison of highest occupied $2p\pi_g^*$ MO for the ground state, $X^3\Sigma_g^-$, and the electronically excited $a^1\Delta_g$ and $b^1\Sigma_g^+$ states.

# Selection Rules

Selection rules tell us something about the probability that a transition will occur.

For atoms: $\Delta S = 0$, $\Delta L = \pm 1$

$$O(^3P) \rightarrow O(^1D)$$
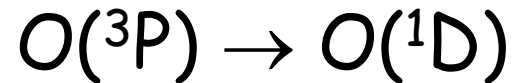
S=1             S=0

L=1             L=2

"spin forbidden" – low probability, long lifetime

# Selection Rules

For molecules: $\Delta S = 0$, $\Delta \Lambda = \pm 1$, $g \rightarrow u$, $+ \rightarrow +$

TABLE 3.1    Allowed[a] Electronic Transitions of Diatomic Molecules Having Light Nuclei[b]

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

[a] Presuming that the rule $\Delta S = 0$ is obeyed.
[b] Source: Herzberg (1950), p. 243.

# Selection Rules

- If all conditions are met,
    - Large transition moment
    - Large absorption cross section
    - Short lifetime
- If all conditions are not met,
    - "forbidden"
    - Can occur, but transition moment is small and lifetime is long.
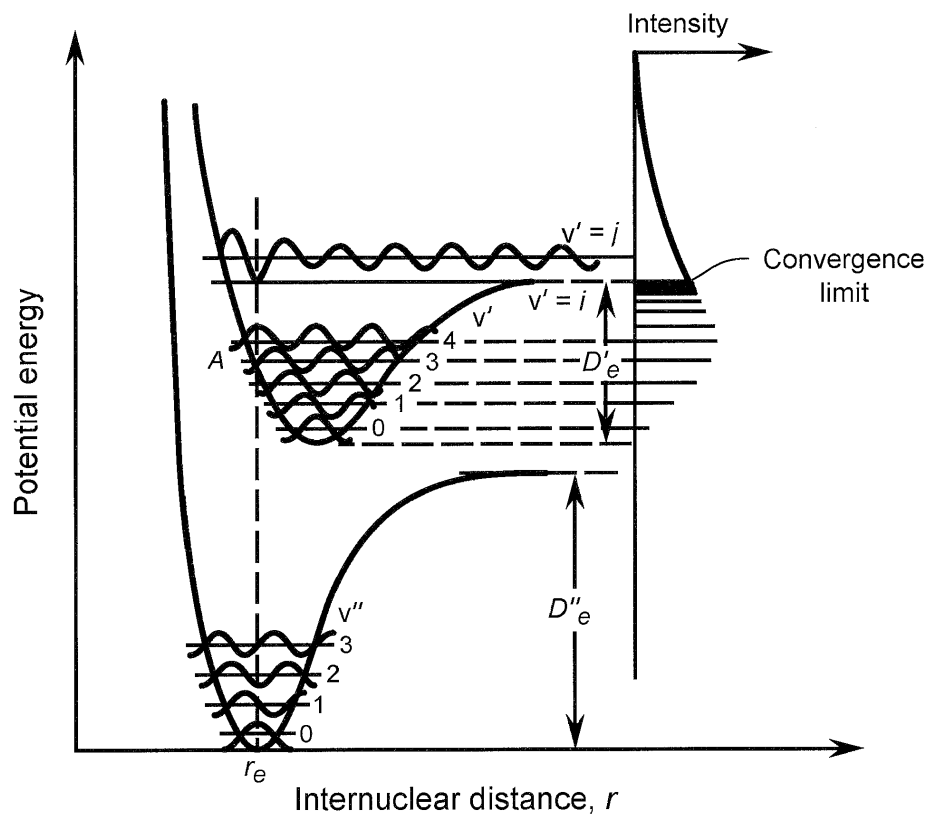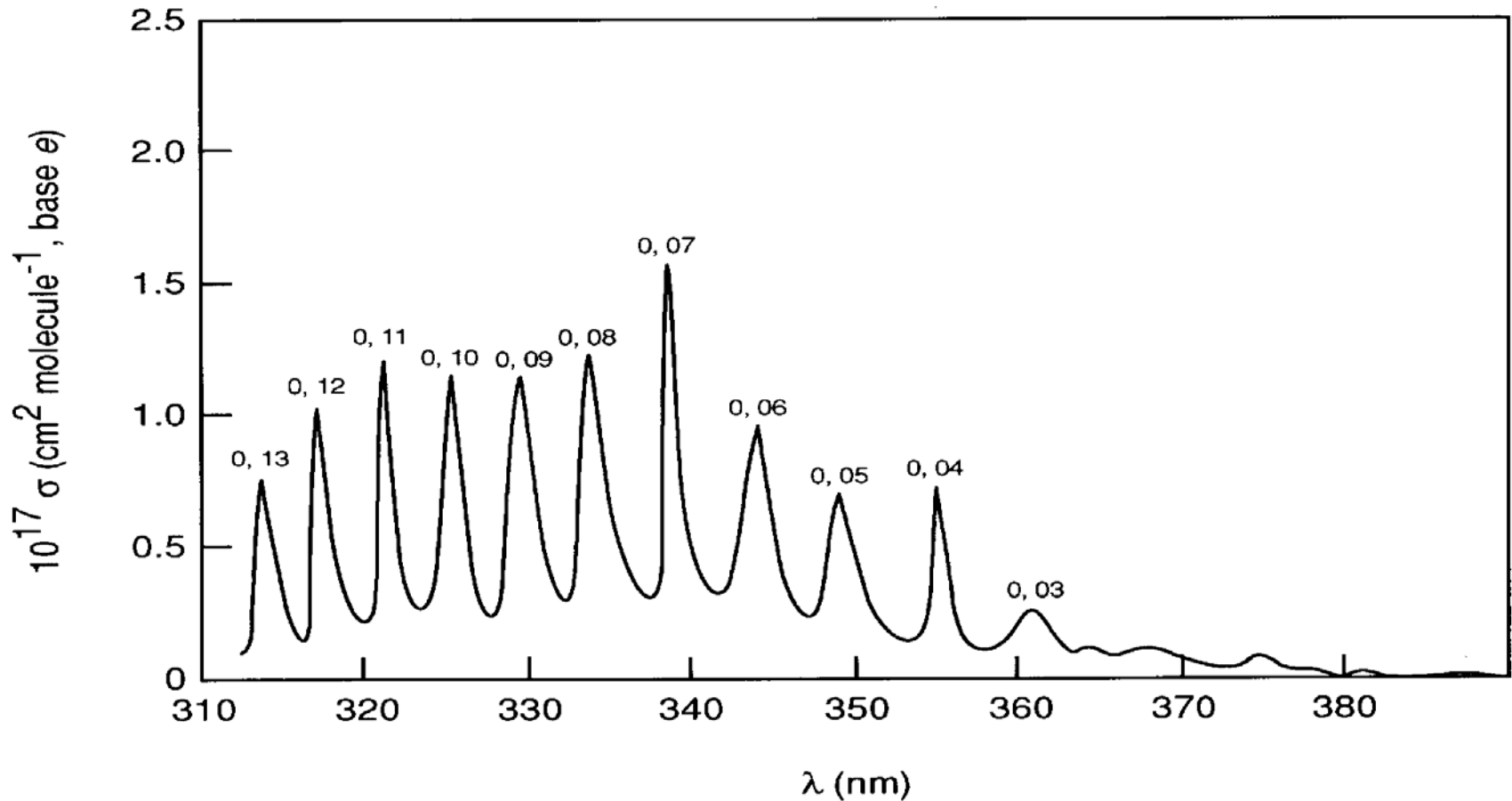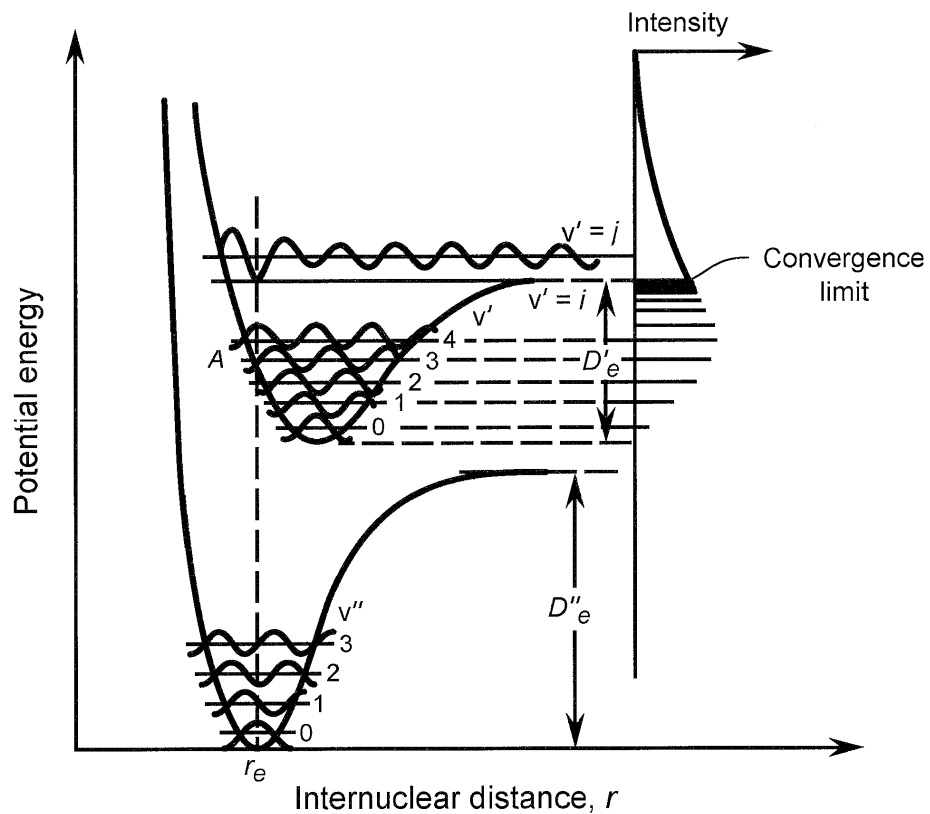
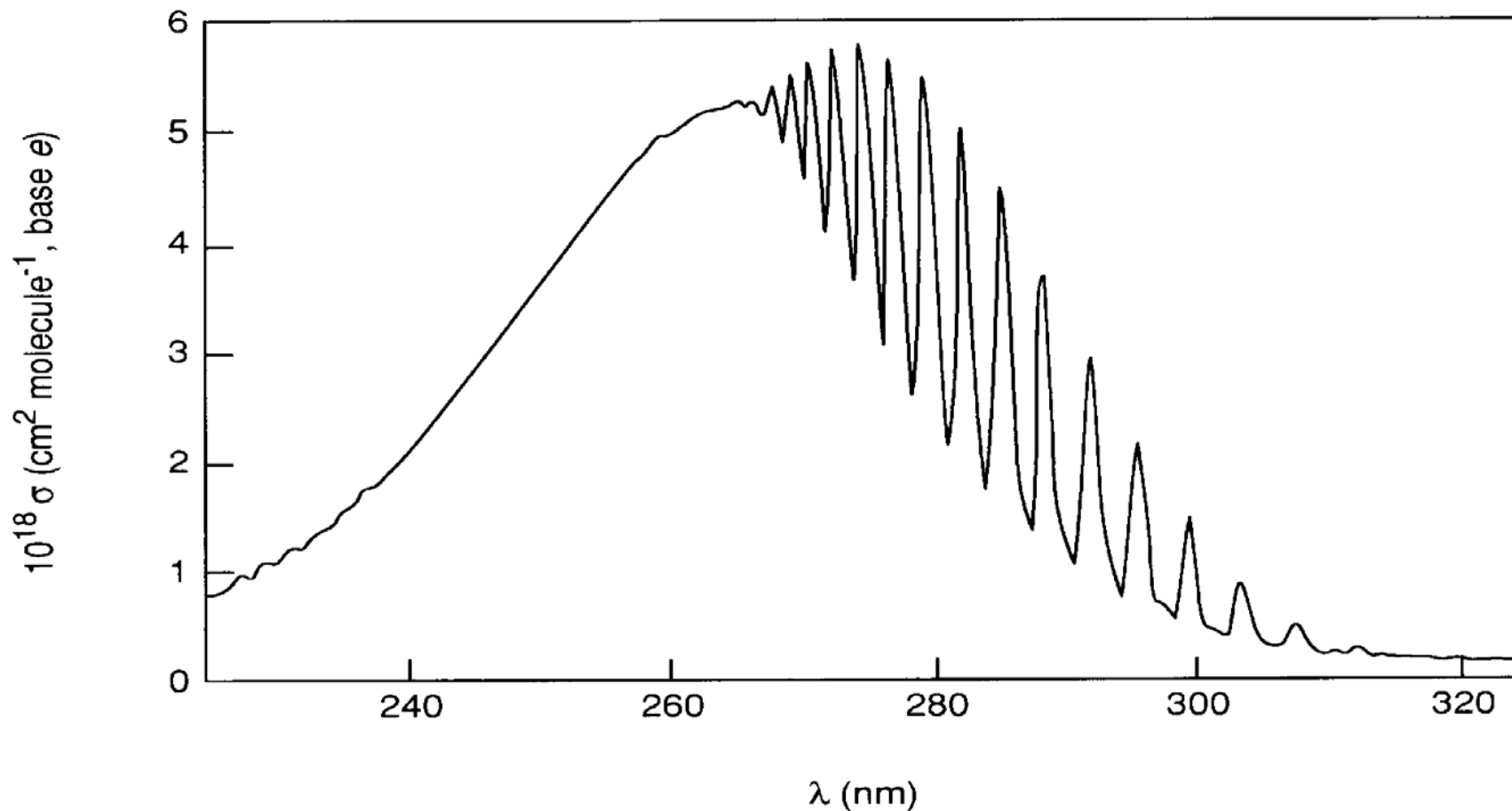# Potential Energy Surfaces



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).

# Vertical Transitions - BrO



**FIGURE 4.36** Absorption spectrum of BrO at room temperature (adapted from Wahner *et al.*, 1988).

# Potential Energy Surfaces



**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).

# Continuum plus bands: ClO



**FIGURE 4.35** Absorption spectrum of ClO (adapted from DeMore *et al.*, 1997).

# Repulsive surfaces
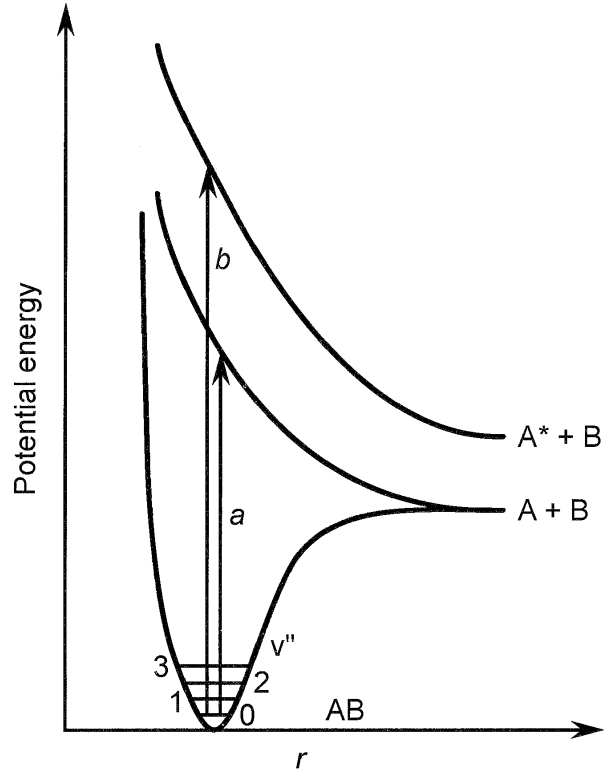


FIGURE 3.7  Potential energy curves for a hypothetical diatomic molecule showing electronic transitions to two repulsive excited states having no minima. A* is an electronically excited atom.
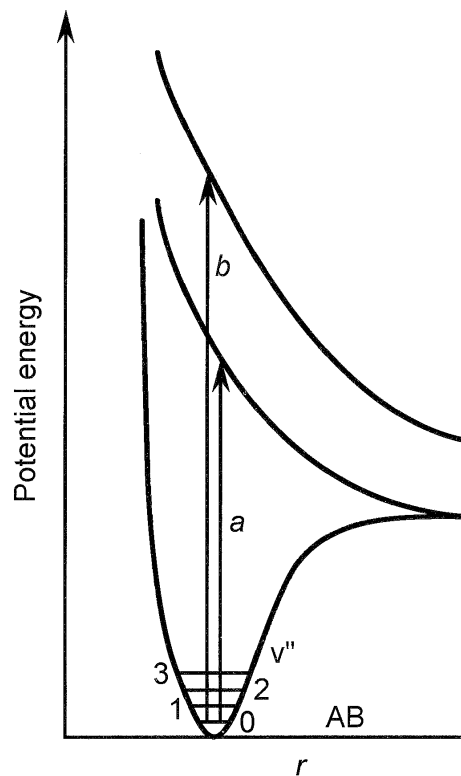
# Repulsive surfaces



FIGURE 3.7 Potential energy curves for a molecule showing electronic transitions to states having no minima. A* is an electronicall
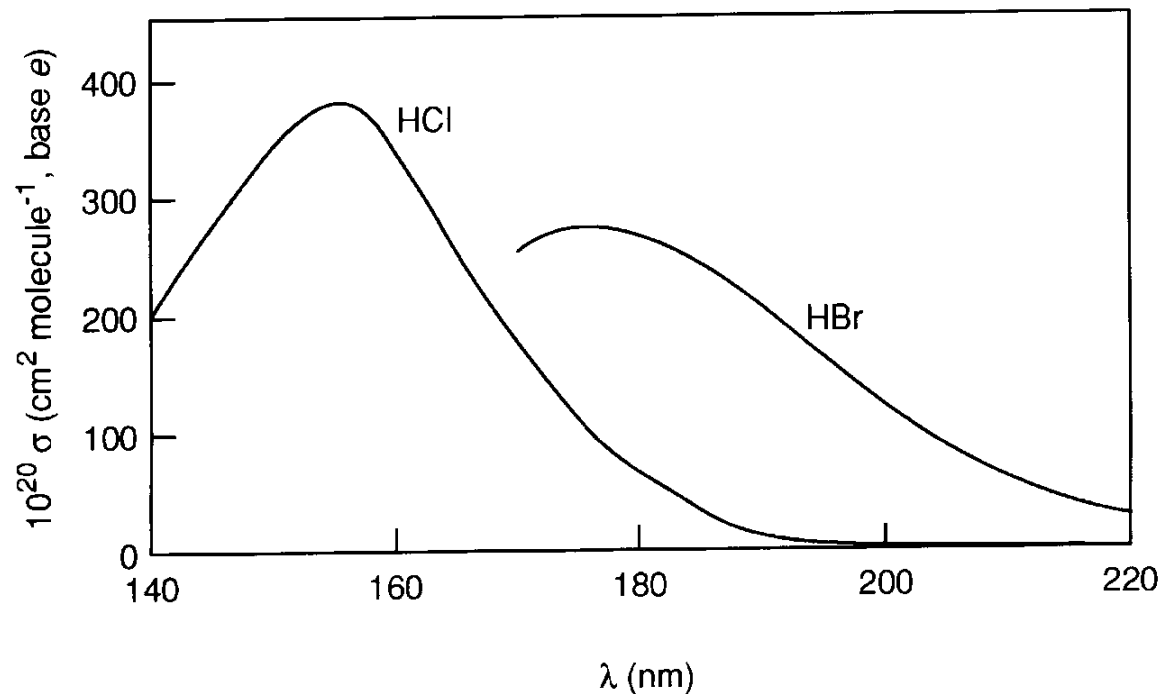
FIGURE 4.33 Absorption spectra of HCl and HBr at room temperature (based on data in DeMore *et al.*, 1997, and Huebert and Martin, 1968).
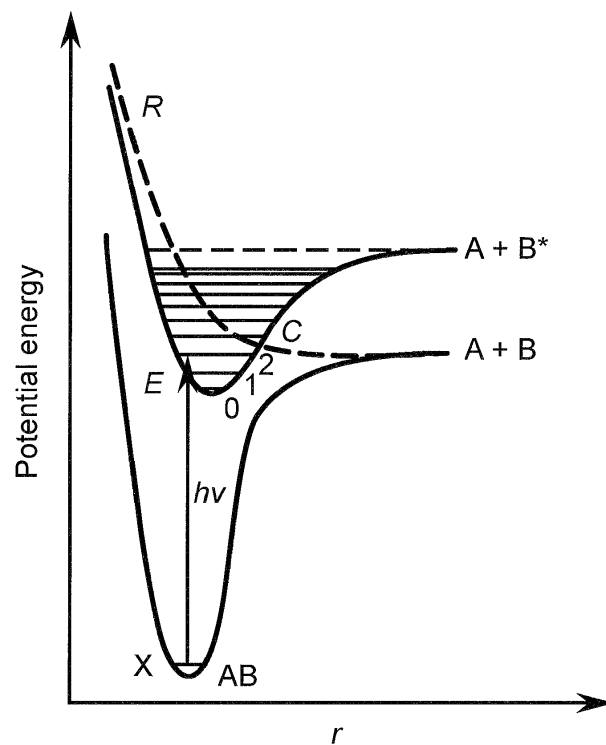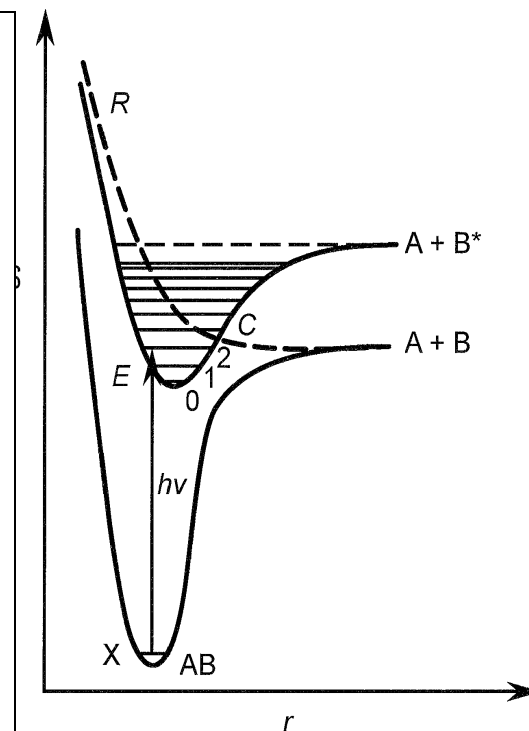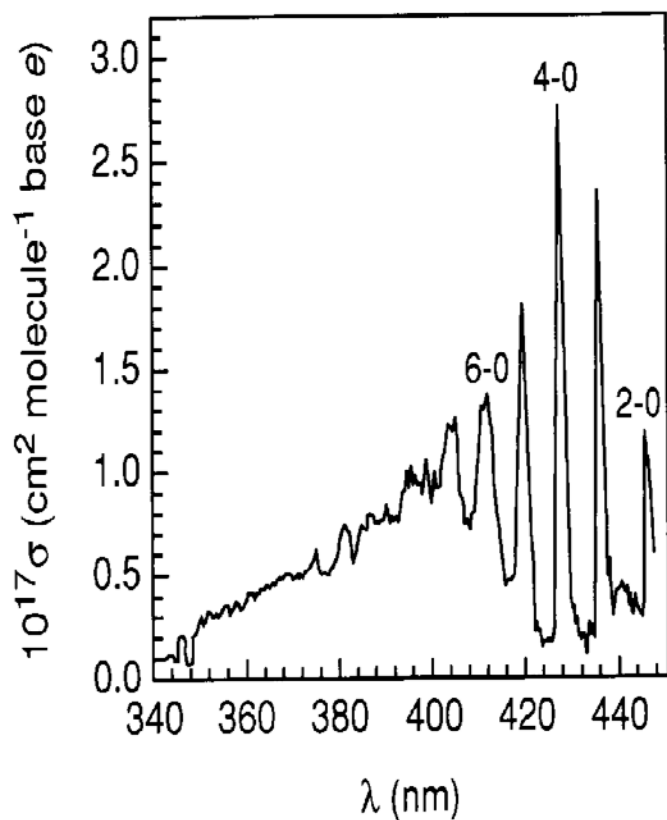
# Predissociative surfaces



**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).
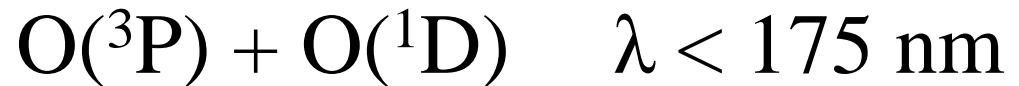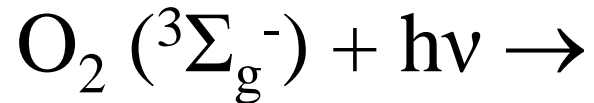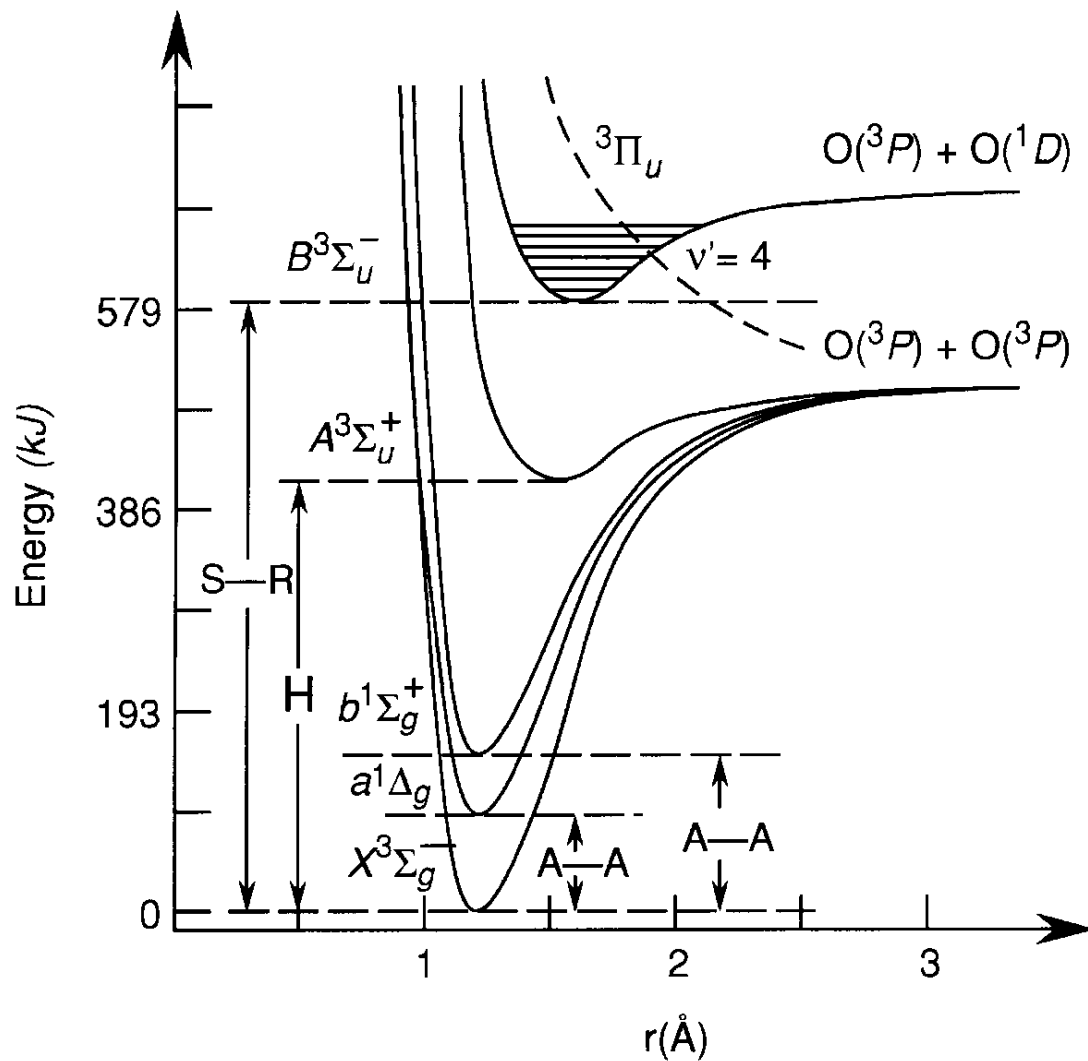
# Predissociative surfaces



FIGURE 4.37 Absorption spectrum of IO at room temperature (adapted from Laszlo *et al.*, 1995).



8 Potential energy curves for the ground state and two excited states in a hypothetical diatomic molecule. on may occur when the molecule is excited into higher vels of the state E and crosses over to repulsive state R C (from Okabe, 1978).

# A final example – $O_2$

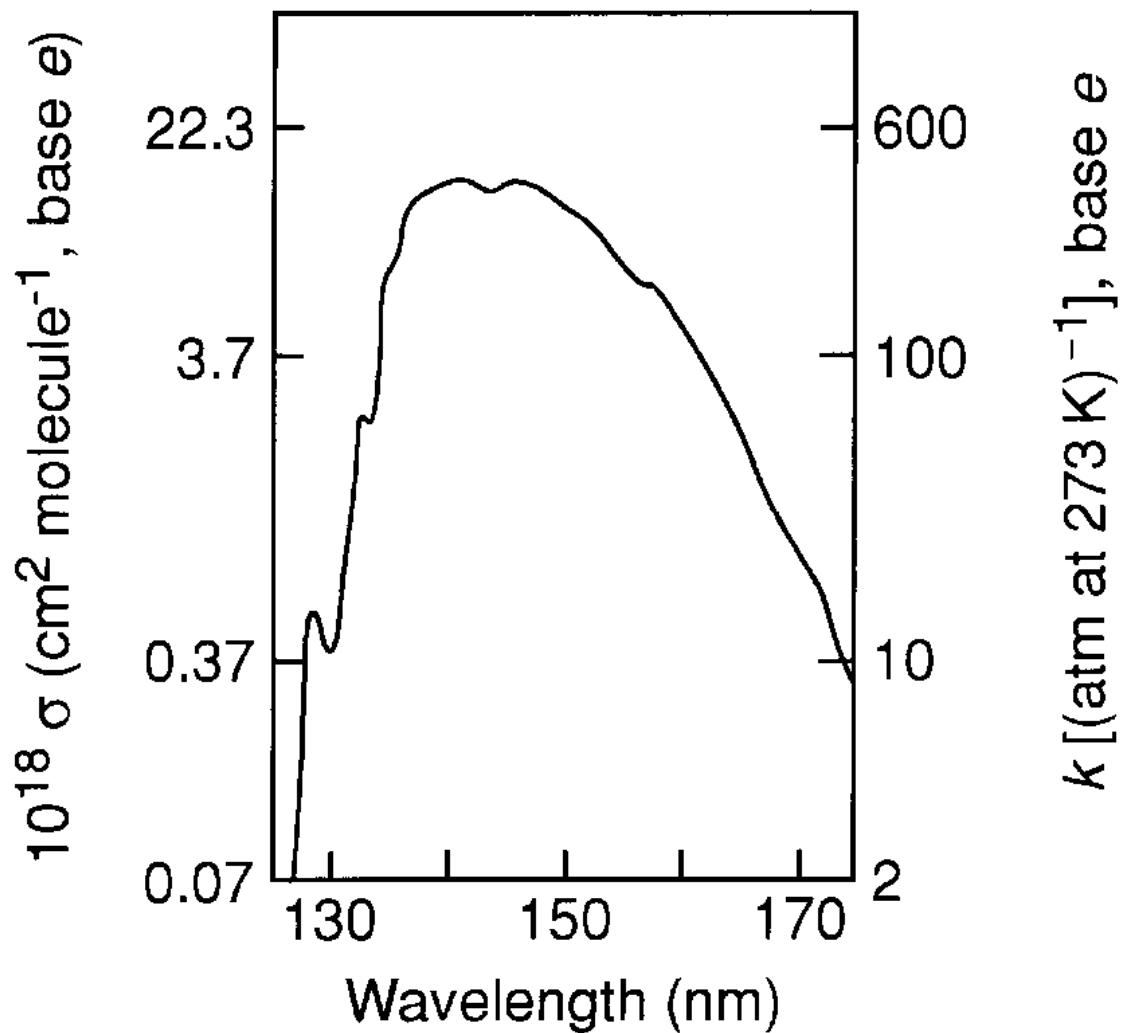$$O_2\ (^3\Sigma_g^-) + h\nu \rightarrow \begin{cases} O\ (^3P) + O(^3P) & \lambda < 242\ \text{nm} \\ \\ O(^3P) + O(^1D) & \lambda < 175\ \text{nm} \end{cases}$$
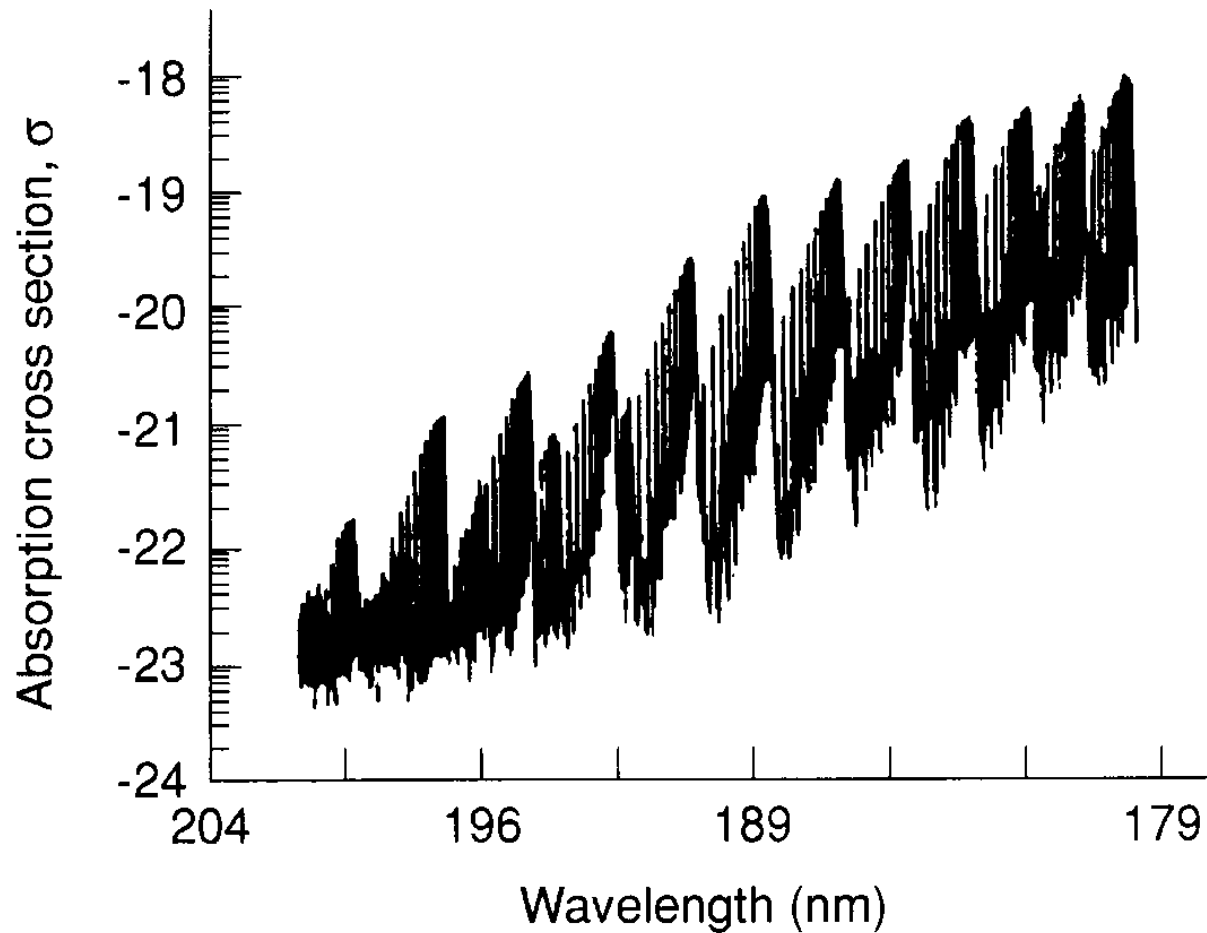
**FIGURE 4.1** Potential energy curves for ground and first four excited states of $O_2$. S–R = Schumann–Runge system, H = Herzberg continuum, A–A = atmospheric bands (adapted from Gaydon, 1968).

FIGURE 4.2 Absorption coefficients for $O_2$ in the Schumann–Runge continuum. Note log scale. (Adapted from Inn, 1955.)

**FIGURE 4.3** Semilogarithmic plot (base 10) of measured absorption coefficients in terms of the absorption cross section, $\sigma$ (cm$^2$ molecule$^{-1}$), base $e$, for $O_2$ at 300 K in the 179.3- to 201.5-nm region. The structure seen for $\sigma > 10^{-22}$ cm$^2$ molecule$^{-1}$ is real; at smaller cross sections, some noise is present (adapted from Yoshino *et al.*, 1992).
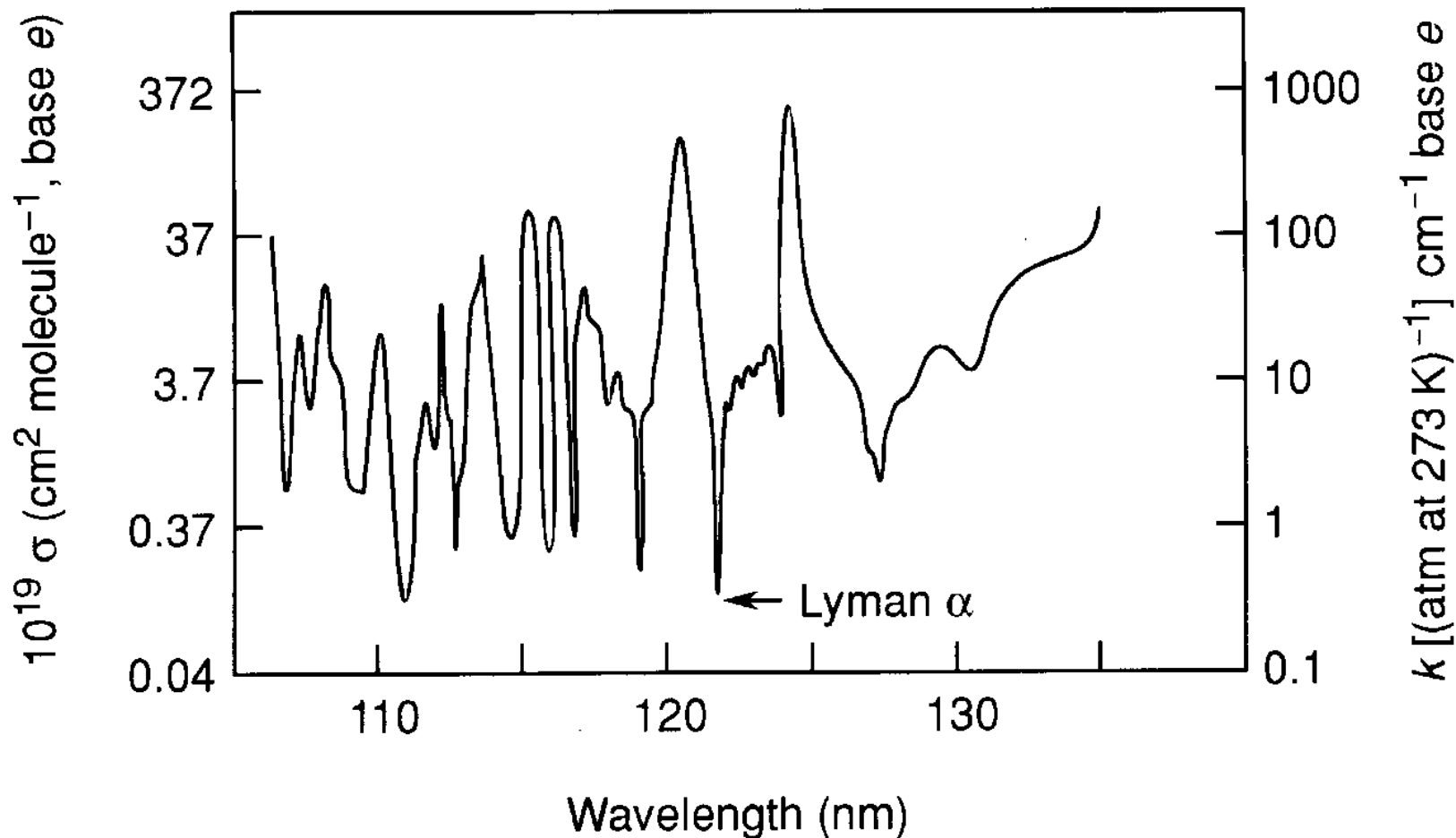
**FIGURE 4.4** Absorption coefficients of $O_2$ in the 105- to 130-nm region. The $O_2$ absorption line corresponding to the Lyman $\alpha$ line of the H atom is shown by the arrow. Note the log scale: Absorption coefficient $k$ on right is for units of [atm at 273 K]$^{-1}$ cm$^{-1}$. (Adapted from Inn, 1955.)
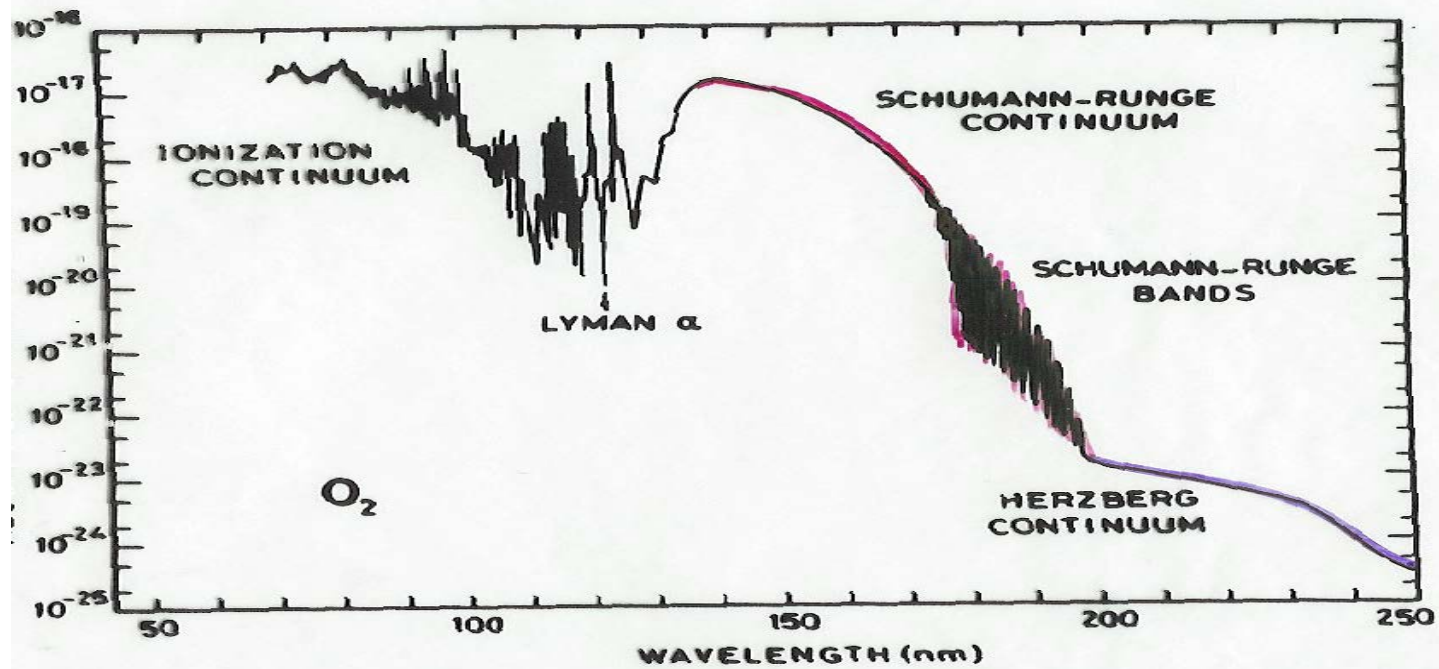
26. Spectral distribution of the absorption cross section of molecular ox-