Chemical spectroscopy

(Chap. 13)

Obj.: general

Study of interaction between light (electromagnetic waves) and matter

location of lines on energy scale
→ energy levels

Improvements of Bohr's theory (QM)
→ levels of larger atoms

Zeeman-effects: interaction of magnetic fields with spin and orbital magnetic momenta

molecules

microwaves, far infrared:
→ rotational lines
→ interatomic distances

near in-frared: higher energy:
→ vibrational + rotational lines
→ force constants of bonds

visible, ultraviolet:

electronic + vibrational + rotational

line systems

→ bonding and antibonding states

molecules: quite complicated spectra, providing much information about chemical structure

atoms: information about levels which are accessible for e^-

<u>further</u>: determination of concentrations

Newton: ≈1665: visible light splits up into a spectrum by a prism (glas)

in matter (glas) the speed of light depends on wavelength: $v(\lambda$

long wavelengths, small frequencies, low energy: red end $\lambda \approx 700\,nm = 7000\,Å$

short wavelength, higher frequencies, high energy: ~~bl~~ violet end $\lambda \approx 400\,nm = 4000\,Å$

<u>units</u>

frequency : ν, unit $1 Hz = 1 s^{-1}$

wavelength : λ, units

$$1 Å = 10^{-8} cm = 10^{-10} m = 0.1 nm$$

$$1 nm = 10^{-9} m$$

$$1 \text{ micron}, \mu = 1 \mu m = 10^{-6} m = 10^{-4} cm$$

$$1 m\mu = 10^{-3} \mu = 10^{-9} m = 10^{-7} cm$$

ν : usually quite large numbers in Hz

vacuum: $c = \lambda \nu$, $c = 2.998 \cdot 10^{8} \frac{m}{s}$

$\lambda = 400 nm \rightarrow \nu = c/\lambda = 7.5 \cdot 10^{14} Hz$

$\rightarrow$ use of wavenumber : $\bar{\nu} = \frac{1}{\lambda}$ (m^{-1}, cm^{-1})

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

m^{-1} : $c = 2.998 \cdot 10^{8} \frac{m}{s}$

cm^{-1} : $c = 2.998 \cdot 10^{10} cm/s$

$$1 cm^{-1} = 100 m^{-1}$$

<u>Emission spectrum</u> system goes from higher energy state (level) to a lower one and emits the energy difference between the states as light ($\Delta E = h\nu$)

→ before an emission spectrum can be observed the system must be excited by a flame or in a discharge tube.

like e.g. H ~~seet~~ spectrum we have discussed

<u>Absorption</u> continous radiation (e.g. white light) passes throug a substance and the system uses light of which $h\nu = \Delta E$ = one of its state energy differences to get excited from a lower to a higher energy level

→ black absorption lines at those frequencies

$\varepsilon = h\nu$: energy of 1 photon

per mole of photons:

$$E = N_A \varepsilon = N_A h\nu = N_A \frac{hc}{\lambda}$$

$$= \frac{6.022 \cdot 10^{23}\,mol^{-1} \cdot 6.626 \cdot 10^{-34}\,Js \cdot 2.998 \cdot 10^{8}\,\frac{m}{s}}{\lambda\,(in\ m)}$$

$\rightarrow E \text{ in } \frac{J}{mol} = 10^{-3} \frac{kJ}{mol}$

if λ in ~~m~~ nm: $E = \frac{1.196 \cdot 10^{5}}{\lambda / nm} \frac{kJ}{mol}$

$\lambda = 400$ nm:

$$E = \frac{1.196 \cdot 10^{5}}{400} \frac{kJ}{mol} = 2.99 \cdot 10^{2} \frac{kJ}{mol}$$

1 einstein: energy of 1 mole photons

for $\lambda = 400$ nm: 1 einstein $= 2.99 \cdot 10^{2} \frac{kJ}{mol}$

light path is splitted through solution and solvent cell: ~~to~~

~~solver~~ solution detector signal
− solvent detector signal

$\rightarrow$ pure solute signals

Sect. on time dep. perturbation theory we cancel. Too ~~m~~ theoretical. Einstein theory shifted to the end of Chap. 13.

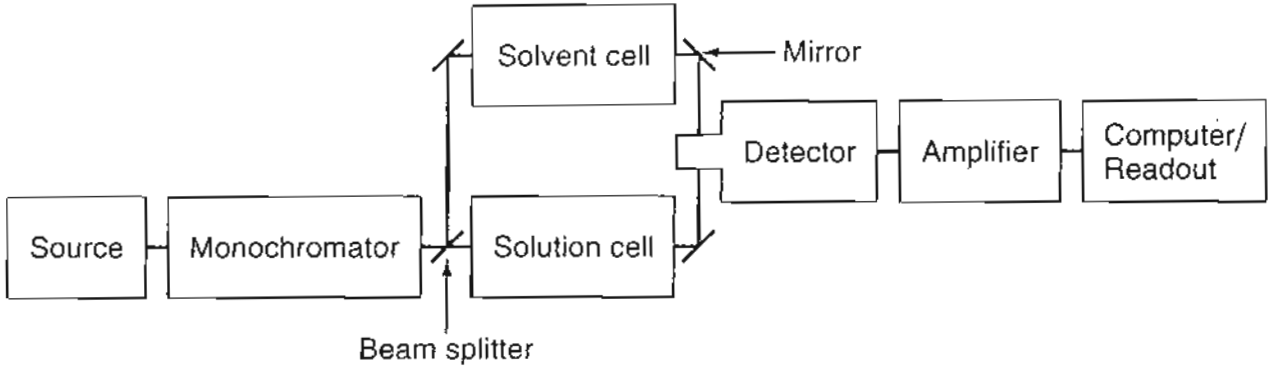

FIGURE 13.1
Schematic of a simple double-beam spectrophotometer. A chopper before the detector may break the light beams so that the detector can tell the difference between the two signals. Alternatively, two matched detectors may be used and the difference measured electronically.

The components of a spectrophotometer change depending upon the region of the spectrum being investigated. A partial listing includes:

For the visible and ultraviolet region: *Source:* tungsten-I_2 lamp or H_2 discharge lamp; *Cell:* Quartz, plastic, or glass; *Detector:* Prism or grating with photomultiplier; *Information:* Electronic spectra.

For the infrared region: *Source:* Hot ceramic source; *Cell:* Sample dispersed in KBr or Nujol, or gas in sample cell; *Detector:* Rock-salt prism or grating with thermocouple detector, or thermistor bolometer (This consists of a semiconductor material whose electrical resistance changes with temperature.) *Information:* Molecular vibration spectra.

EXAMPLE 13.1 Calculate the energy in kJ mol^{-1} corresponding to absorption at 400 nm.

Solution Substitution of $\lambda = 400$ nm into Eq. 13.1 gives 2.99×10^2 kJ mol^{-1}.

The amount of energy absorbed by 1 mol of a compound at a particular wavelength has been called an **einstein** and is the energy of 1 mol of photons at that wavelength. In Example 13.1, 1 einstein equals 2.99×10^2 kJ.

The Laws of Lambert and Beer

When spectroscopic studies of substances are combined with measurements of light absorbed and transmitted at various wavelengths, the term **spectrophotometry** is employed. This type of investigation is based on laws propounded by the German mathematician Johann Heinrich Lambert (1728–1777) and the German astronomer Wilhelm Beer (1797–1850). These laws are concerned with the intensities of light absorbed or transmitted when incident light is passed through some material.

Lambert's law states that the proportion of radiation absorbed by a substance is independent of the intensity of the incident radiation. This [illegible] ssive

ultraviolet / visible (UVIS)

W - I_2 lamps

H_2 discharge lamps

cell: quartz, plastics, glas

detector: prism, photomultiplier

infrared (IR)

hot ceramic as lamps

cell: sample in KBr
or gas in a KBr cell

detector: rock salt prism
or bolometer: material where
resistance $R = f(T)$
IR radiation heats the bolometer

far infrared (FIR)

source: electrical oscillators

cell: cavity

detector: crystal diode
W in contact with a semiconductor

usually : $\varepsilon_\ell^c(\lambda)$

if $c = 1M = 1 \frac{mol}{L}$, $\ell = 1cm$

$\lambda = 430$ nm (violet)

we write $\varepsilon_{1cm}^{1M}(430nm)$

molar absorption coefficient

measure A for different c and ℓ

$\rightarrow \varepsilon$ at a wavelength

$$\varepsilon_\ell^c(\lambda) = \frac{A}{c\ell} \left(\frac{L}{mol\,cm} = \frac{dm^3}{mol\,cm} = 10^3 \frac{cm^2}{mol} \right)$$

purine-triphosphate:

mass concentration 57.8 mg/L

molar mass: $M = 586$ g/mol

$A = 1.014$ at $\ell =$ ~~1cm~~ 1.0 cm

ε_ℓ^c ? A of 10 μM ? T% ?

$$c = \frac{57.8 \cdot 10^{-3}\ g/L}{586\ g/mol} = 0.0986 \cdot 10^{-3} \frac{mol}{L} = 9.86 \cdot 10^{-5}\ M$$

Lambert's law

proportion of absorbed light intensity is independent of the incident intensity I_0

or $-\frac{dI}{I}$ = intensity loss in each sample layer dx

$$\rightarrow -\frac{dI}{I} = b\,dx$$

b is a constant, the absorption coefficient

$$\rightarrow \int_{I_0}^{I} \frac{dI}{I} = -b\int_0^{\ell} dx$$

$$\ln I - \ln I_0 = \ln \frac{I}{I_0} = -b\ell$$

$$\rightarrow I = I_0 e^{-b\ell}$$

decadic log (basis 10)

→ absorbance A:

$$A = \log_{10} \frac{I_0}{I} = \frac{bl}{2.303}$$

transmittance T:

$$T = \frac{I}{I_0}$$

$$A = \log_{10} \frac{I_0}{I} = \log_{10} \frac{1}{T} = -\log_{10} T$$

$$T\% = 100 \cdot T = 100 \frac{I}{I_0}$$

$$\rightarrow \log_{10} T\% = \log_{10} 100 + \log_{10} T = 2 - A$$

<u>Beer's law</u>

similar for concentrations:

$$\log_{10} \frac{I_0}{I} = A = \text{const.} \cdot c$$

→ <u>Lambert - Beer law</u>

$$A = \log_{10} \frac{I_0}{I} = \varepsilon c l$$

ε: absorption coefficient: constant but depends on λ

l: light path length

usually : $\varepsilon_\ell^c(\lambda)$

if $c = 1M = 1 \frac{mol}{L}$, $\ell = 1cm$

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23 - 10

$$\varepsilon = \frac{A}{c\,l} = \frac{1.014}{9.86 \cdot 10^{-5}\,M \cdot 1.0\,cm}$$

$$= 1.028 \cdot 10^{4}\,\frac{dm^3}{mol\,cm}$$

at $10\,\mu M$

$$A(\mu M) = \varepsilon c l = 1.028 \cdot 10^{4}\,\frac{dm^3}{mol\,cm} \cdot 10 \cdot 10^{-6}\,M \cdot 1.0\,cm$$

$$= 1.028 \cdot 10^{-1} = 0.1028$$

$$\log_{10} T\% = 2 - A = 1.8972$$

$$\rightarrow T\% = 10^{1.8972} = 78.9\,\%$$

Time-dependent perturbation theory

stationary states: $\psi(x,y,z,t)$

$$= \psi(x,y,z)\, e^{-Et/\hbar}$$

→ time-independent Schrödinger eq.:

$$\hat{H}\psi_i = E_i \psi_i$$

assume we know all eigenvalues E_i and eigenstates ψ_i

<u>no</u> degenerate levels (more easy)

$$\psi_i^0 = \psi_i\, e^{-iE_i t/\hbar}$$

+ electromagnetic field, EM, ?

transitions $i \leftrightarrow k$?

for transition $i \to k$, coupling must exist ψ_i, ψ_k, EM

oscillating dipol moments emit light (e.g. black body)

general: molecules and atoms have electric and magnetic moments

→ coupling to EM: E^0, H^0 of EM

electric dipole moment along x

from separation of charges δq by x

$$\mu_x = x\,\delta q$$

μ(el.) interact with E^0

μ(mag.) with H^0 of EM

here only μ(el.) treated.

coupling small → perturbation

$$[\hat{H} + \hat{H}'(t)]\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

$$\hat{H}'(t) = 2\hat{\mu}_x E_x^0 \cos \omega t$$

amplitude → frequency

EM mixes eigen states (transition)

→ no pure eigenstate but

$$\Psi = \sum_i c_i(t)\,\Psi_i^0(t)$$

no EM: $\hat{H}'(t) = 0$ → pure eigenstate

with EM: starting from pure Ψ_i^0,

mixing with other, Ψ_k^0, occurs

(transition)

probability to find system in k after

time t: $c_k^*(t)c_k(t) = |c_k(t)|^2$

$t=0$: pure $\psi_i^0(0)$

$\rightarrow c_i(0) = 1$, $c_k(0) = 0$ for $k \neq i$

$c_k(t)$

$$[\hat{H} + \hat{H}'(t)]\psi = i\hbar \frac{\partial \psi}{\partial t}$$

$$= i\hbar \frac{\partial}{\partial t} \sum_i c_i(t)\, \psi_i^0$$

$$= i\hbar \sum_i \frac{\partial c_i(t)}{\partial t} \psi_i^0 + i\hbar \sum_i c_i(t) \frac{\partial \psi_i^0}{\partial t}$$

$$i\hbar \frac{\partial \psi_i^0}{\partial t} = \hat{H} \psi_i^0$$

$$[\hat{H} + \hat{H}'(t)]\psi = i\hbar \sum_i \frac{\partial c_i(t)}{\partial t} \psi_i^0 + \sum_i c_i(t) \hat{H} \psi_i^0$$

$$\psi = \sum_i c_i(t)\, \psi_i^0(t)$$

$$\rightarrow \sum_i c_i(t)\, \hat{H} \psi_i^0 = \hat{H}\psi$$

$$\rightarrow [\hat{H} + \hat{H}'(t)]\psi = i\hbar \sum_i \frac{dc_i(t)}{dt} \psi_i^0 + \hat{H}\psi$$

$$\hat{H}'(t)\, \psi = i\hbar \sum_i \frac{dc_i(t)}{dt} \psi_i^0$$

$$\sum_i c_i(t) \hat{H}' \psi_i^0 = i\hbar \sum_i \frac{dc_i(t)}{dt} \psi_i^0$$

$$\int (\psi_k^0)^* \psi_i^0 \, d\tau = \delta_{ki} = \begin{cases} 1, & k = i \\ 0, & k \neq i \end{cases}$$

$\rightarrow$ multiply by $(\psi_k^0)^*$ and integrate:

$$\sum_i c_i(t) \int (\psi_k^0)^* \hat{H}'(t) \psi_i^0 \, d\tau$$

$$\uparrow$$

$$dx\,dy\,dz$$

$$= i\hbar \sum_i \frac{dc_i(t)}{dt} \int (\psi_k^0)^* \psi_i^0 \, d\tau$$

$$= i\hbar \sum_i \frac{dc_i(t)}{dt} \delta_{ik} \qquad \delta_{ik} = \begin{cases} 1, & i = k \\ 0, & i \neq k \end{cases}$$

$$= i\hbar \frac{dc_k(t)}{dt} \qquad \frac{1}{i} = \frac{i}{i^2} = -i$$

$$\frac{dc_k(t)}{dt} = -\frac{i}{\hbar} \sum_i c_i(t) \int (\psi_k^0)^* \hat{H}'(t) \psi_i^0 \, d\tau$$

$$\psi_i^0 = \psi_i e^{-iE_i t/\hbar} \qquad (\psi_k^0)^* = \psi_k^* e^{E_k t/\hbar}$$

$$\frac{dc_k(t)}{dt} = -\frac{i}{\hbar} \sum_i c_i(t) e^{i(E_k - E_i)t/\hbar} \int \psi_k^* \hat{H}'(t) \psi_i \, d\tau$$

exact!

1. order perturbation theory approximation:

transition between 2 isolated levels: $c_i(t)$, $c_k(t)$

all others: $c_j(t) = 0$, $j \neq i$, $j \neq k$

and $c_i(0) = 1$, $c_j(0) = 0$, $j \neq i$

for <u>any</u> level k:

$$\frac{dc_k(t)}{dt} = -\frac{i}{\hbar} c_i(t) e^{-i(E_k - E_i)t/\hbar} \langle \psi_k | \hat{H}'(t) | \psi_i \rangle$$

<u>very</u> weak perturbation

→ all $c_k(t)$ $(k \neq i)$ never become large

→ $c_i(t) \simeq c_i(0) = 1$ at all times

$$\rightarrow \quad c_k(t) = -\frac{i}{\hbar} \int_0^t e^{-i(E_k - E_i)t/\hbar} \langle \psi_k | \hat{H}'(t) | \psi_i \rangle dt$$

time dependence in $\hat{H}'(t)$ (EM-wave)

$$\cos \omega t = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$$

→ time dependence of the integrand:

$$f_{ik}(\omega, t) = \frac{1}{2} e^{\frac{i(E_k - E_i)t}{\hbar}} (e^{i\omega t} + e^{-i\omega t})$$

$$\rightarrow \quad c_k(t) = -\frac{i}{\hbar} E_x^0 \langle \psi_k | \hat{\mu}_x | \psi_i \rangle \int_0^t f_{ik}(\omega, t)\, dt$$

energy density w:

$$w = \frac{3}{2} \varepsilon_0 (E_x^0)^2_{aver.}$$

→ integration with $c_k(0) = 0$:

$$c_k^*(t)\, c_k(t) = \frac{1}{\hbar}\left[\langle \psi_k | \hat{\mu}_x | \psi_i \rangle\right]^2 (E_x^0)^2_{av} \cdot t$$

→ a $i \to k$ transition is forbidden, if the <u>matrix element</u>

$$\langle \psi_k | \hat{V} | \psi_i \rangle = \int \psi_k^* \hat{V} \psi_i \, d\tau = 0$$

$\hat{V}$ ↓ perturbation, e.g. $\hat{\mu}_x$

→ selection rules

Bohr condition:

$$E_k - E_i \approx \hbar\omega$$

ω: frequency of emitted ~~and~~ or absorbed photon

if <u>not</u>: $\int_0^t f_{ik}(\omega, t)\, dt$ <u>very</u> small ≈ 0

Obj. exchange, spin-orbit, vector model (24) - 1
near infrared: close to visible

$7 \cdot 10^{-7} - 2 \cdot 10^{-4}$ m $\qquad \lambda >$ red

vacuum UV: $\lambda < 200$ nm

Vacuum needed for spectra:

H_2O in air absorbs there

high resolution multiple lines can turn to single lines in low resolution spectra (simple spectrometers)

H $\quad$ 2s — — — — $\qquad E_n$

1s —

more e^-: Coulomb repulsion between them

— — — 2p

→ 2s —

Term symbol: like s, p, d orbitals ($l = 0, 1, 2$)

but: S, P, D, $L = 0, 1, 2$

for terms (states)

L: total angular momentum of many e^-

<u>in H</u>: $L = \sqrt{l(l+1)}\,\hbar$ (1 e⁻)

<u>many e⁻</u>: $L = \sum_i l_i$ vector addition

→ angular momentum $\sqrt{L(L+1)}\,\hbar$

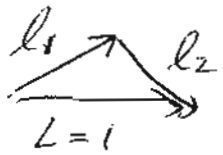
<u>H</u>: $n=1,\ l=0$: s / $n=2,\ l=0,1$, s, p

$n=3,\ l=0,1,2$, s, p, d

<u>2e⁻</u>: angles between the vectors l_1 and l_2 can only be such, that the result of vector addition must be an integer L

$l_1 = 1,\ l_2 = +1$: ↑↓ $L = 0$ s
180°

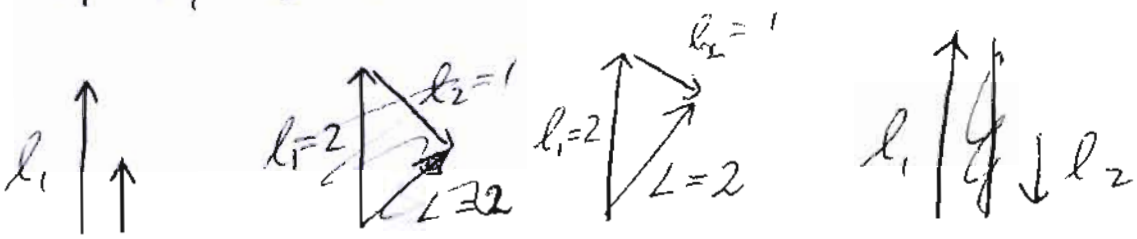
$l_1 = 1,\ l_2 = 1$



P ↑↑ $L=2$, D

all sides equal

$l_1 = 2,\ l_2 = 1$



$L=3$ F

only 2 equal sides possibl

D

$L=1$ P

~~He: $1s^2$~~

Exchange interaction

spin-correlation

He $1s^2$ $\uparrow\downarrow$ following Pauli: 2e in 1orb. possible, but opposite spin

$1s^1\ 2s^1$ $\uparrow\uparrow$ or $\uparrow\downarrow$ possible

Hund: lower higher energy

m_s of each e^-: $+\frac{1}{2}$ or $-\frac{1}{2}$

resulting spin quantum number:

$$S = \sum_i m_{s_i}$$

multiplicity: $2S+1$ no. of possible spin functions for S

vector addition

$$\left.\begin{array}{ll} \alpha(1)\,\alpha(2) & m_{s_1} + m_{s_2} = 1 \\ \alpha(1)\,\beta(2) + \alpha(2)\,\beta(1) & m_{s_1} + m_{s_2} = 0 \\ \beta(1)\,\beta(2) & m_{s_1} + m_{s_2} = -1 \end{array}\right\} \begin{array}{l}\text{Triplet} \\ S=1\end{array}$$

symmetric functions

$$\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1) \quad m_{s_1} + m_{s_2} = 0 \quad \begin{array}{l}\text{Singlet} \\ S=0\end{array}$$

1e $\uparrow$ $m_s = \frac{1}{2}$, $\rightarrow S = \frac{1}{2} \rightarrow M = 2S+1 = 2$

$\downarrow$ multiplicity (24) - 4

doublet

2e $\uparrow\uparrow$ $m_{s_1} = \frac{1}{2}$, $m_{s_2} = \frac{1}{2} \rightarrow S = 1$ $M = 2S+1 = 3$

triplet

or $\uparrow\downarrow$ $m_{s_1} = \frac{1}{2}$, $m_{s_2} = -\frac{1}{2} \rightarrow S = 0$ $M = 2S+1 = 1$

singlet

3e $\uparrow\uparrow\uparrow$ all $m_s = \frac{1}{2}$, $S = \frac{3}{2} \rightarrow 2S+1 = 4$

quartet

or $\underbrace{\uparrow\uparrow}_{1/2}\underbrace{\downarrow}_{-1/2}$ $S = 1 - \frac{1}{2} = \frac{1}{2} \rightarrow M = 2$ doublet

H : $l = 0 \Rightarrow L = 0$, $S = \frac{1}{2} \rightarrow 2S+1 = 2$

$\Rightarrow$ H has a ^{2}S state ($2S+1$; $L = 0$)

multiplicities in $1s^2 2s^2 2p^2$

paired electrons (filled subshells) cancel

$\Rightarrow$ only $2p^2$ count because $1s^2$, $2s^2$ are filled subshells

$\longrightarrow$ $S = 1$ $\underset{+1/2}{\uparrow}$ $\underset{+1/2}{\uparrow}$ _ $\Rightarrow$ triplet: $2S+1 = 3$

or $S = 0$ $\underset{+1/2}{\uparrow}$ $\underset{-1/2}{\downarrow}$ _ $\Rightarrow$ singlet: $2S+1 = 1$

$l_1 = 1, \; l_2 = 1$

$\Rightarrow L = 0, 1, 2 : \; {}^1S, \; {}^1P \; {}^1D$ spin singlets

or ${}^3S, \; {}^3P, \; {}^3D$ spin triplets

exchange interaction:

simplest in He $\rightarrow$ level splitting

$1s^2 : \; l_1 = l_2 = 0 \Rightarrow L = 0, \; S = 0 \; (\uparrow\downarrow)$

$\Rightarrow 1 \, {}^1S$ ground state

$n = 1$ $\quad$ $\rightarrow 2S+1 = 1$ $\quad$ $\rightarrow L = 0$

excited state: $1s^1 2s^1$ or $1s^1 2p^1$

$L = 0 : S \qquad L = 1 : P$

2e can be a spin singlet $(S=0)$

or a spin triplet $(S=1)$

$\Rightarrow$ states $\quad 2\,{}^1S, \; 2\,{}^1P$

possible: $\quad 2\,{}^3S, \; 2\,{}^3P$

Hund: $E_{2\,{}^3S} < E_{2\,{}^1S}$

$E_{2\,{}^3P} < E_{2\,{}^1P}$

${}^1S: \; E_1 = J + K$

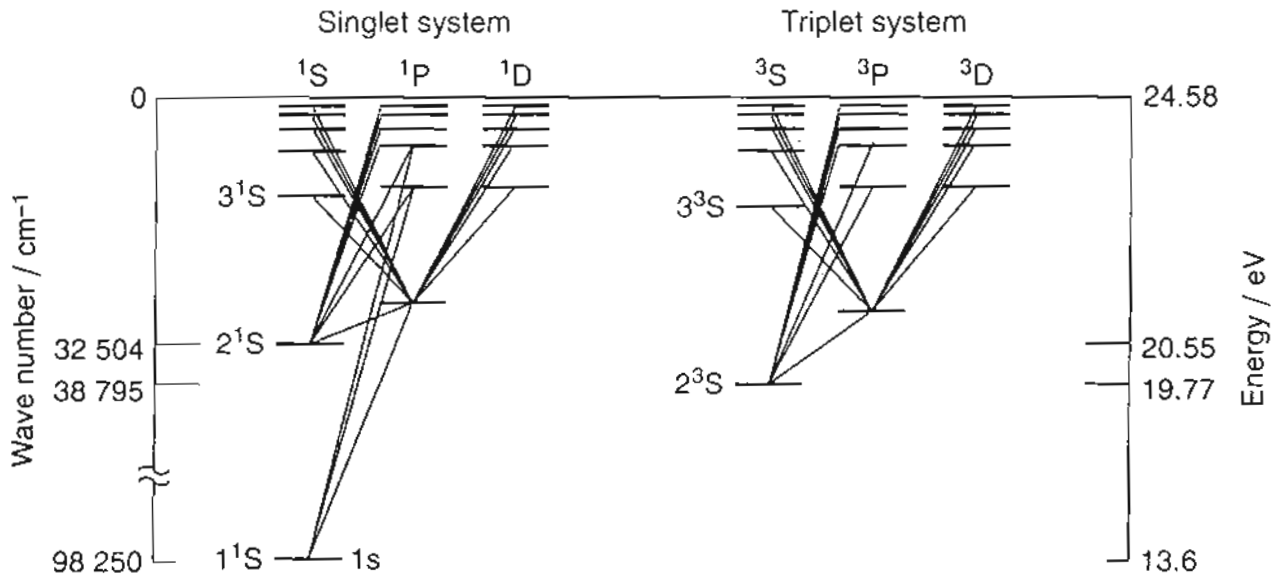
${}^3S: \; E_3 = J - K$

difficult to calculate, but can be measured in spectrum

The way in which exchange interaction (spin correlation) brings about the splitting of energy levels can be illustrated by the simplest atom that shows this effect, namely helium. The term diagram of helium is shown in Figure 13.4, in which the terms are divided into two sets. At one time these were thought to arise from two distinct forms of helium, *parahelium* and *orthohelium*, but this is now known not to be the case. The first set consists of *singlets* (multiplicity = 1) and the other of *triplets* (multiplicity = 3). The ground state of helium is $1s^2$ with $L = 0$ ($l_1 = 0, l_2 = 0$) and $S = 0$ since the electrons must have opposite spins. Hence its ground-state term symbol is ^1S.

If one electron is promoted to $n = 2$, two possibilities exist, $1s^12s^1$ and $1s^12p^1$. The first of these has $L = 0$ and is an S state. The second has $L = 1$ and is a P state.

ergy-level diagram for
ing the singlet and
ystems.



spin-orbit interactions

~~the~~ Coulomb and Exchange terms are there not in H, because only 1e!

but

Balmer series: $(n>2) \to n=2$

left higher energy level

$\to$ direction $\to$ emission

$\leftarrow$ absorption

low resolution: $n=3 \to n=2$ lowest Balmer line

1 line in low resolution

high resolution: 7 lines

magnetic coupling between orbit and spin magnetic moments

$\to$ spin-orbit interactions

in H: l-s coupling to

total momentum $j = l \pm s$

~~S-state~~ s state: $l=0 \to$ only $j=\frac{1}{2}$

($j=-\frac{1}{2}$ makes no difference)

selection rules:

allowed, possible, ~~spec~~ transitions:

$$\Delta n = \pm 1, \pm 2, \ldots$$

$$\Delta l = \pm 1$$

$$\Delta j = 0, \pm 1$$

fulfilled by all transitions between 3S and 3P:

$3^2S_{1/2} \not\rightarrow 2^2S_{1/2}$ $\quad S \rightarrow S$: $l: 0 \rightarrow 0$, but $\Delta l = \pm 1$

$\rightarrow$ 7 possible transitions: (Balmer: $n = 3 \rightarrow 2$)

$3^2P_{1/2} \rightarrow 2^2S_{1/2}$ $\quad \Delta j = 0, \Delta l = -1$

$3^2S_{1/2} \rightarrow 2^2P_{1/2}$ $\quad \Delta j = 0, \Delta l = 1$

$3^2D_{3/2} \rightarrow 2^2P_{3/2}$ $\quad \Delta j = 0, \Delta l = -1$

$3^2D_{5/2} \rightarrow 2^2P_{3/2}$ $\quad \Delta j = -1, \Delta l = -1$

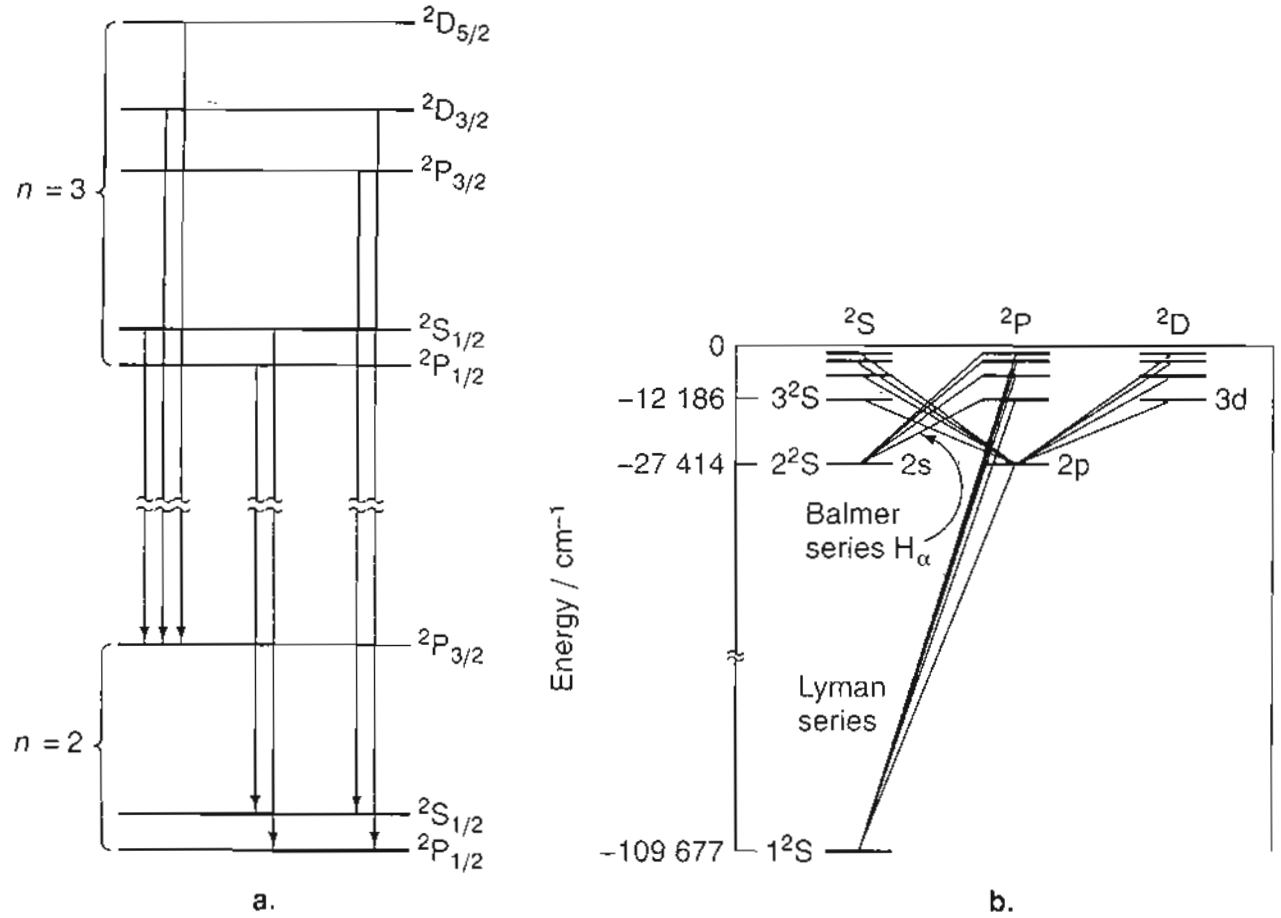
$3^2S_{1/2} \rightarrow 2^2P_{3/2}$ $\quad \Delta j = -1, \Delta l = 1$

$3^2D_{3/2} \rightarrow 2^2P_{1/2}$ $\quad \Delta j = -1, \Delta l = -1$

$3^2P_{3/2} \rightarrow 2^2S_{1/2}$ $\quad \Delta j = -1, \Delta l = -1$

all others forbidden!

example: $3^2D_{5/2} \rightarrow 2^2P_{1/2}$ $\quad \Delta l = 1, \underline{\underline{\Delta j = 2}}$



URE 13.5
States associated with the line ($n_1 = 2 \leftrightarrow n_2 = 3$) of the mer series for the hydrogen m spectrum, as detected by h-resolution spectroscopy. (b) A plified energy diagram for the rogen atom, showing various sitions. This type of diagram now as a Grotrian diagram, ned for Otto Natalies August trian (1847–1921).

to Eq. 13.19, we have

$n = 1$: $^2S_{1/2}$

$n = 2$: ^2S ^2P ^2D

Russell-

<u>Lyman series</u> $(n>1) \rightarrow n=1$

$2\,^2S_{1/2} \not\rightarrow 1\,^2S_{1/2}$ $\Delta l = 0$

$2\,^2P_{1/2} \nearrow$ $\nwarrow 2\,^2P_{3/2}$ 2 allowed

true for most Lyman lines (only 2)

because D or higher to $1\,^2S_{1/2}$: $\Delta l \neq \pm 1$

difficult to observe in

H-Lyman spectra

<u>easy in Na</u>: ~~sta~~ strongest yellow lines

$\rightarrow$ 589.0 nm

589.6 nm

Do <u>not</u> learn energy positions of terms: can be obtained only by calculation or measurements not by general arguments

LS term symbol: $n\,^{2S+1}L_j$

<u>Selection rules</u>. $\Delta n = \pm 1, \pm 2, \ldots$

many e atoms: $\Delta L = \pm 1$ $\Delta J = 0, \pm 1$

$\Delta S = 0$

<u>Obj</u> still vector model

e^-, like we on earth see the sun going roundes, see the nucleus like it rotates around the e^-

→ magnetic field by nucleus

→ l_i, s_i vectors align

<u>light atoms</u> Russel-Saunders coupling or LS coupling occurs:

1) add the spin momenta of the electrons vectorial:

$s = \sum m_{s_i}$ → integer or half-integer

2 electrons (even no. of e^-):

$s = 0, 1$

3 electrons (odd no. of e^-):

$s = \frac{1}{2}$ or $\frac{3}{2}$ $\uparrow\uparrow\uparrow = 3/2$ $\uparrow\downarrow\uparrow = 1/2$

2) add vectorial the orbital momenta l_i for each e-

$\rightarrow L$

<u>then</u> 3) total angular momentum $J = L + S$

with $|J| = \sqrt{J(J+1)}\,\hbar$

J integer or half-integer

L and S coupling strong

$\rightarrow$ distant levels in energy

L S coupling to J weak

$\rightarrow$ closely spaced J levels

<u>Selection rules:</u>

$\Delta S = 0$

$\Delta L = \pm 1$

$\Delta J = 0, \pm 1$ (besides ~~$J=0 \rightarrow J=0$~~ which is ~~forbidden~~)

since photons have 1 spin momentum

$\rightarrow J=0 \rightarrow J=0$ transition <u>not</u> allowed

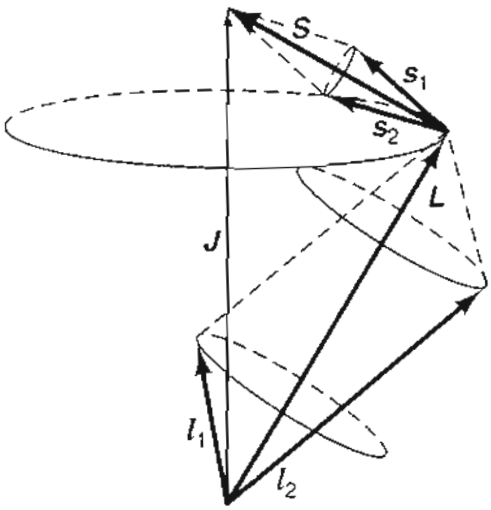


FIGURE 13.6
Precession of ***L*** and ***S*** about ***J*** for Russell-Saunders coupling. The individual ***l*** couple and ***s*** couple form resultant ***L*** and ***S*** *before* coupling to form ***J***.

absence of an external field, L and S prece
keep the total angular momentum a constant a
coupling, J precesses relatively more slowly a

In Russell-Saunders coupling, which appl
L and to form S is strong. This means that th
states of considerably different energies. On t
to form J is weak, resulting in J values that d

The selection rules that apply to transition
summarized as

$$\Delta S = 0$$
$$\Delta L = 0, \pm$$
$$\Delta J = 0, \pm$$

There is a further restriction, known as the *Lapo*
with odd terms:

$$g \not\leftrightarrow g \qquad u \not\leftrightarrow u$$

This is a symmetry effect. In addition

$$J = 0 \not\leftrightarrow J =$$

The underlying reason behind these selection r
of spin angular momentum; there therefore mu
when a photon is absorbed or emitted.

j-j Coupling

For heavy atoms (i.e., for atoms of high a
of coupling, known as ***j-j* coupling.** The spin-o
cause the individual l and s vectors for each ele
vectors. These in turn couple to form a total J f
explained in terms of enhanced spin-orbit inter
outermost electrons by all the remaining electro
changes very rapidly as a function of distance f
penetrates deeply into the shielding electron c
number of electrons, there is an increase in th
magnetic field felt by an electron in a heavy ato

<u>heavy atoms</u> jj coupling

for <u>each</u> electron <u>first</u> couple l with s to yield j for each e^-

<u>then</u> couple all j_i to J

because valence e^- in large shielding cloud of inner ones

for jj coupling: S, L are no good (unimportant) quantum numbers

→ other selection rules in jj cases

singlet – triplet excitations are allowed in heavy atoms

$$S = 0 \rightarrow S = 1$$

for closed shells: no contribution

$$L = S = J = 0$$

22

2 electrons with $L > S$

non-equivalent e^-

$L = (l_1 + l_2), (l_1 + l_2 - 1), \dots, (l_1 - l_2)$ $L > 0$

$S = (s_1 + s_2), (s_1 - s_2) = 0, 1$

$J = (L+S), (L+S-1), \dots, (L-S)$

if n and l are the same (equivalent electrons) more difficult

Zeeman effect

<u>normal</u> splitting of spectral lines in magnetic fields because orbit momentum only (occurs only in spin-singlet states)

<u>anomalous</u>: also spins involved

more common!

e^- in circular orbit, radius r, velocity u

$\rightarrow$ circles/unit-time : $\frac{u}{2\pi r}$

= passing of a fixed point/unit time

→ current $I = -e\frac{u}{2\pi r}$

EM theory. magnetic moment

$$\mu_\ell = \text{current} \cdot \text{area}$$

$$\mu_\ell = -\frac{eu}{2\pi r}\pi r^2 = -e\frac{ur}{2}$$

left hand rule: fingers of left hand in circle direction, thumb points in μ_ℓ direction

μ_ℓ perpendicular to the circle

angular moment opposite to μ.

$$L = m_e u r$$

→ gyromagnet or magnetogyric ratio:

$$\gamma = \frac{\mu_\ell}{L} = -\frac{eur}{2m_e ur} = -\frac{e}{2m_e}$$

L_z along field direction

(direction of z-axis free

→ can always be put into field direction

$L_z = m_\ell \hbar$

$\mu_{\ell z} = \pm L_z \cdot \gamma = m_\ell \frac{e\hbar}{2m_e}$ $\quad m_\ell = \pm l, \pm(l-1), \dots, 0$

Bohr magneton: $\mu_B = \frac{e\hbar}{2m_e} = 9.274 \cdot 10^{-24}\ Am^2$

$\mu_{\ell z} = m_\ell \mu_B$

magnetic field strength: $H\left(\frac{A}{m}\right)$

magnetic flux density: $B\left(\frac{kg}{As} = \frac{Vs}{m^2} = T\right)$

Tesla

$E = \mu_{\ell z} B$

energy of magn. moment $\mu_{\ell z}$ in field

$\rightarrow E = m_\ell \mu_B B = m_\ell \frac{e\hbar}{2m_e} B$

$\rightarrow [\mu_B] = \frac{J}{T} = Am^2$

$J \rightarrow VAs$, $T \rightarrow \frac{Vs}{m^2}$

$2l+1$ possible m_ℓ values

$\rightarrow$ each level ~~splitt~~ split into $2l+1$ components

energy seperation of 2 consecutive levels: $\Delta E = \mu_B B \sim B$

independent of m_ℓ

H-atom in field with $B = 1T$ (25) - 7

wavelength splitting for $n=3 \rightarrow n=2$

transition = lowest Balmer line (656.2 nm)

$$\Delta E = \mu_B B = 9.274 \cdot 10^{-24} \frac{J}{T} \cdot 1T = 9.274 \cdot 10^{-24} J$$

$$= 5.79 \cdot 10^{-5} eV$$

$$E_{n=3} - E_{n=2} = \underset{R_y}{13.6 eV} \left(-\frac{1}{9} + \frac{1}{4} \right) = 1.9 eV$$

fractional energy change

$$= \frac{5.8 \cdot 10^{-5} eV}{1.9 eV} \approx 3 \cdot 10^{-5}$$

for 656.2 nm:

$$\Delta\lambda = 656.2 nm \cdot 3 \cdot 10^{-5} = 0.02 nm$$

can be easily measured

for atoms with more e^-:

$$l, \Delta m_e \supset L, \Delta M_L$$

$^1S_0$: $L = S = 0 = J$ no splitting, singlet state

$^1P_1$: $L = J = 1 \longrightarrow M_L = +1, 0, -1$

singlet P

spin singlet

→ $^1P_1 \rightarrow {}^1S_0$ yields 3 lines in B-field

$^1D_2 \rightarrow {}^1P_1$ also 3 lines in field (equal spacing of levels)

normal Zeeman effect for singlet states

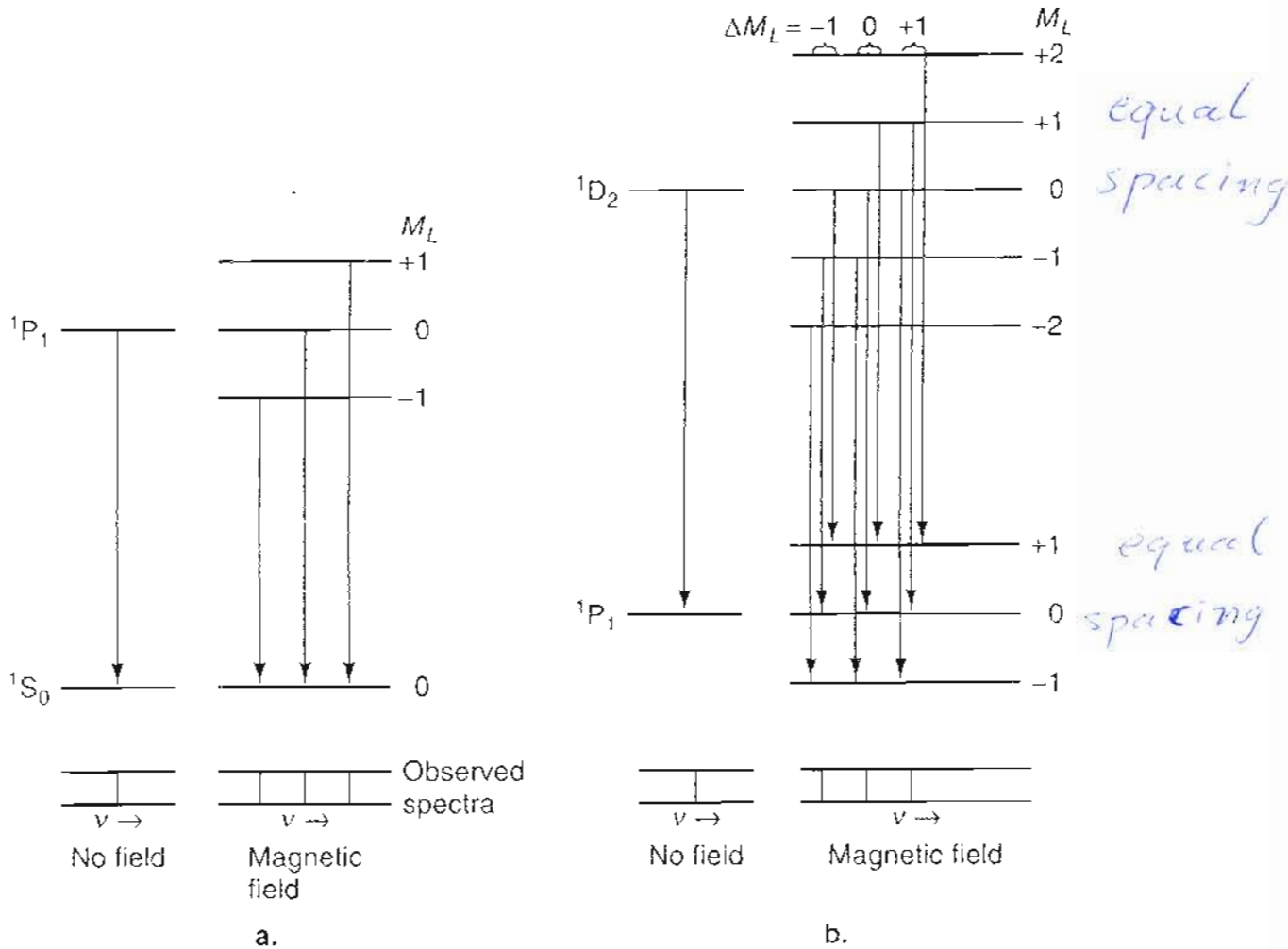


FIGURE 13.7
The normal Zeeman effect, arising from the interaction of the orbital angular momentum with a magnetic field. (a) The $^1P_1$–$^1S_0$ transition, where the $^1P_1$ state is split into three levels so that three Zeeman lines are observed. (b) The $^1D_2$–$^1P_1$ transition. Because the split levels are equally spaced, there are still only three Zeeman lines.

The energy of a magnetic dipole μ_z in a magnetic field is

$$E = \mu_z B \tag{13.50}$$

and therefore each energy level in the atom is split into the values

$$E = g_L M_L \mu_B B \tag{13.51}$$

anomalous effect $S > 0$

L-S coupling $\rightarrow J$

$\rightarrow \mu_J = g_J M_J \mu_B$

$\rightarrow E = g_J M_J \mu_B B$

g_J: Lande g-factor:

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

g_J between 0 and 2

$^3S_1$: $g_J = 2.0023$

$^3P_0$: $g_J = 0$ $\quad$ $^3P_1, {}^3P_2$: $g_J = \frac{3}{2}$

in high fields more complicated

spacing of levels in S and P

not equal because g_J different

$$^3P_1: g_J = 1 + \frac{1\cdot 2 + 1\cdot 2 - 1\cdot 2}{4} = 1 + \frac{1}{2} = \frac{3}{2}$$

$$^3P_2: g_J = 1 + \frac{2\cdot 3 + 2\cdot 2}{4\cdot 2\cdot 3} = 1 + \frac{1}{2} = \frac{3}{2}$$

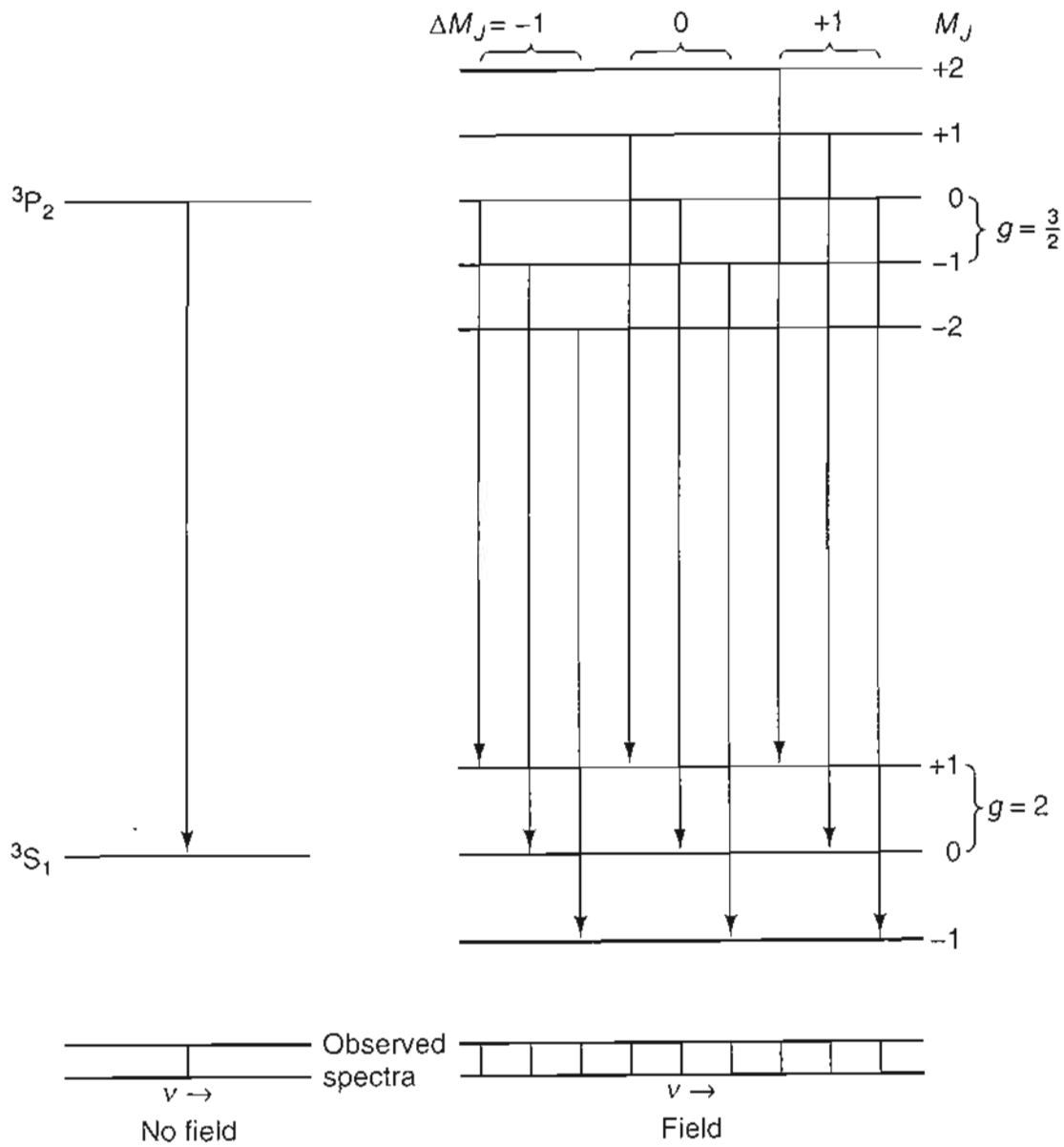


FIGURE 13.8
The anomalous Zeeman effect for the transition $^3P_2$–$^3S_1$.

EXAMPLE 13.6 Into how many levels will a $^3D_2$ level split in a magnetic field?

Paschen - Back effect

<u>high</u> fields B

→ coupling B with J

≫ coupling of L to S

→ L, S uncoupled and rotating ~~along~~ around the field uncoupled

→ triplets as in normal Zeemen effect (as S=0 only L) but each of the three lines has <u>closely</u> spaced components (because of small L-S coupling)

Paschen - Back effect:

high magn. fields

J to field coupling > L-S coupling

→ lines back to normal triplets

but closely spaced splitting

Into how many levels is a $^3P_2$ state split in a magn. field?

if $B = 4T$: separation of neighboring levels?

$^3D_2$: $J = 2$, $L = 2$ (D), $S = 1$ ($2S+1 = 3$)

$M_J = \pm 2, \pm 1, 0$ 5 levels

$$g_J = 1 + \frac{2 \cdot 3 + 1 \cdot 2 - 2 \cdot 3}{2 \cdot 2 \cdot 3} = 1.167$$

$$E = g_J M_J \mu_B B$$

$$= 1.167 \cdot 9.273 \cdot 10^{-24} \frac{J}{T} \cdot 4T \cdot M_J$$

$\Delta M = 1$:

$$\Delta E = 1.167 \cdot 9.273 \cdot 10^{-24} \cdot 4 \; J = 4.329 \cdot 10^{-23} J$$

separation in cm^{-1}:

$$\Delta\bar{\nu} = \frac{\Delta E}{hc} \qquad c = 2.998 \cdot 10^{10}\ \frac{cm}{s}$$

gives cm^{-1}

$$\rightarrow \Delta\bar{\nu} = 2.18\ cm^{-1}$$

Pure rotational spectra

in atoms: only electronic transitions

molecules:

Born-Oppenheimer:

$$E = E_e + E_v + E_r$$

→ E_e (diatomics): neglect of vibrations (R_0 = const.) (E_v)

E_r: again r_0 = const. to calculate the moment of inertia I

(again vibrations neglected)

Microwave, far IR (FIR):
only simple rotational spectra

near IR: vibrational transitions and rotational transitions
energy of vib transition always enough to have also rot. ones
more complex

visible, UV: electronic transitions
+ all others (E_v, $E_r \ll E_e$) most complex

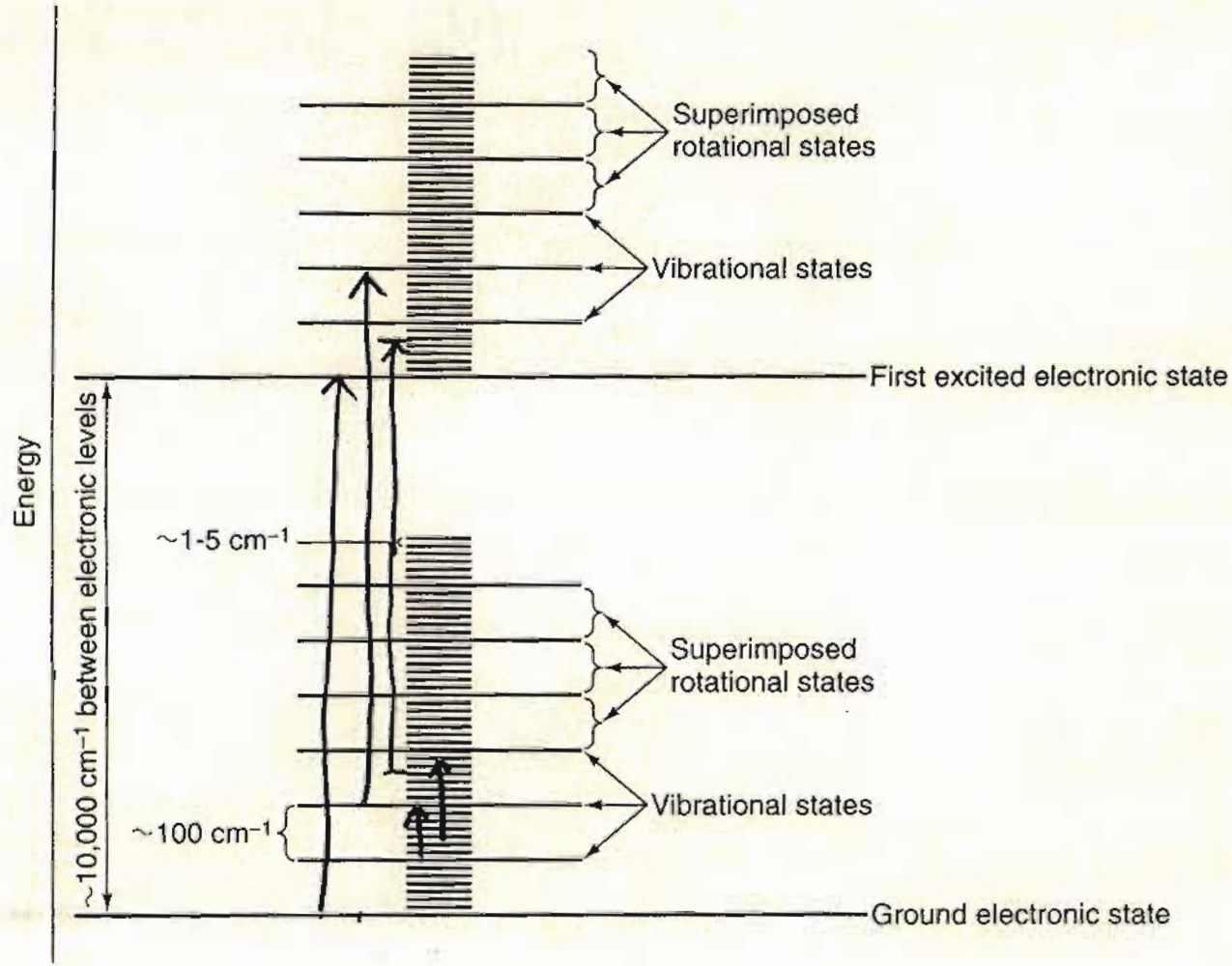


FIGURE 13.9
Typical energy separations for rotational, vibrational and electronic levels. As permitted by the Born-Oppenheimer approximation, the energy is separated into the three types, so that rotational levels are superimposed on vibrational levels and vibrational levels on electronic levels.

energy of a diatomic molecule we can take the distance between the nuclei to be the equilibrium distance, as if the molecule were not vibrating. Similarly, in dealing with rotations we can consider only the equilibrium internuclear distances when we calculate moments of inertia.

of rotational and vibrational energy. As a result, molecular spectra are considerably more complicated than atomic spectra, because in a molecule a transition may involve simultaneous changes in electronic, vibrational, and rotational energy. However, some simplification is brought about by the fact that the amount of energy involved in a pure rotational transition is considerably less than that in a change of vibrational state, which in turn involves less energy than a change of electronic state. An indication of the different energies and of the spectral regions where each type of transition occurs is given in Table 13.1. The relationships between the different types of motion are illustrated in Figure 13.9, in which rotational levels are superimposed on vibrational levels, and vibrational levels are superimposed on electronic levels.

Born-Oppenheimer Approximation

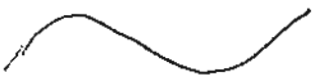
In representing the situation as we do in Figure 13.9 we are making use of the **Born-Oppenheimer approximation** (see also Section 12.1). When we try to solve the exact Schrödinger equation, which takes into account different forms of energy, the energy cannot be separated into rotational, vibrational, and electronic contributions. However, Max Born and J. R. Oppenheimer were able to show that by neglecting certain very small terms in the equation the separation can be made, so that the total energy E is the sum of the electronic energy E_e, the vibrational energy E_v, and the rotational energy E_r. This means, for example, that in dealing with electronic

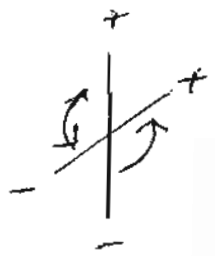
TABLE 13.1 Types of Optical Spectra

Spectroscopic Region	Approximate Range: Frequency s^{-1}	Approximate Range: Wave Number cm^{-1}	Approximate Range: Energy $kJ\ mol^{-1}$	Types of Molecular Energy	Information Obtained
Microwave and far infrared	10^9–10^{12}	0.03–30	4×10^{-4}–0.4	Rotation	Interatomic distance and rotational constants
Infrared	10^{12}–10^{14}	30–3000	0.4–40	Vibration and rotation	Interatomic distances and force constants of bonds
Visible and ultraviolet	10^{14}–10^{16}	3×10^3–3×10^5	40–4000	Electronic, vibration, and rotation	Electronic energy levels, bond dissociation energies, force constants of bonds, and interatomic distances

rotational transitions can be observed in spectra <u>only</u> if the molecule has a permanent dipole moment

$\vec{E}$ of a wave





rotation = oscillating dipole

permanent partial charges necessary for interaction with $\vec{E}$ of the wave

→ linear molecules with inversion center ($D_{\infty h}$) have no dipole moment (for dipole the atoms must be different) and <u>no</u> rotational spectra

e.g. N_2, C_2H_2 no dipole moments

$C_{\infty v}$: no inversion:

HF, HCN dipole moments

→ rotational spectra

diatomic molecules

from rigid rotor:

angular momentum $L = \sqrt{J(J+1)}\,\hbar$

$J = 0, 1, 2, \ldots$ rotational quantum number

$E_J = J(J+1)\frac{\hbar^2}{2I}$ I: moment of inertia

as in H atom: $m_\ell = -\ell, \ldots, -1, 0, 1, \ldots +\ell$

$2\ell+1$ degenerate levels

E_J: $2J+1$ degenerate levels

angular momentum vector $\underline{J}$:

$2J+1$ different orientations to a fixed axis possible

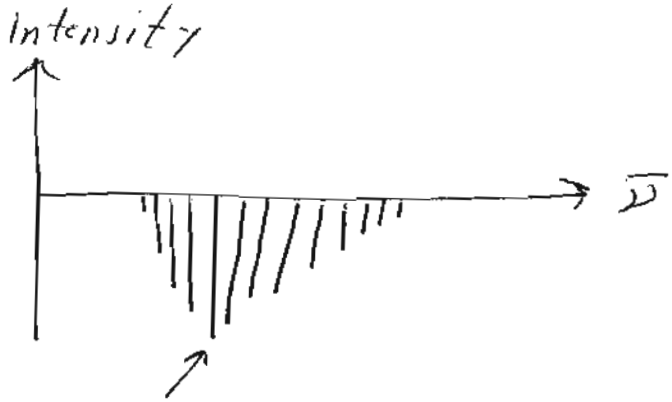
Intensity ~ population of the starting state with rotating molecules

Boltzmann factor: $e^{-\frac{E_J}{k_B T}}$

each energy E_J has this population

degeneracy factor: $2J+1$ levels with E_J

population of a state of energy $E_J \sim (2J+1)e^{-\frac{E_J}{k_B T}}$



observed mostly in absorption

population maximum at starting state

<u>in linear molecules</u>

moment of inertia around the axis of a linear molecule $I = 0$ (z)

if rotation occurs around any other axis $\perp$ (90°), e.g. x or y

the moment around a rotation axis through the center of mass and perpendicular to the molecular axis:

$$I = m_1 r_1^2 + m_2 r_2^2$$

r_1 distance from m_1 to center of mass

The rotational spectrum of a diatomic mol
molecule to be a rigid rotor. The solution of t
(Section 11.10; Eq. 11.208) shows that the
given by the equation

$$L = \sqrt{J(J+1)}\frac{h}{2\pi}$$

where J is the rotational quantum number. Tl
by Eq. 11.209,

$$E_J = J(J+1)\frac{h^2}{8\pi^2 I}$$

where I is the moment of inertia and J can ha

Each rotational level with quantum numb
arises in the same way that the m_l values come
the hydrogen atom. That is, the angular momer
along the Z axis may have $2J+1$ different
space with respect to a fixed axis. Each of the s
equally probable. A **statistical weighting fact**
each rotational level. The relative population of
tor and also on the Boltzmann factor (Eq. 15.34
decreases as the energy increases. The combin
intensity of the rotational states to initially incre
increases.

Statistical Weighting Factor

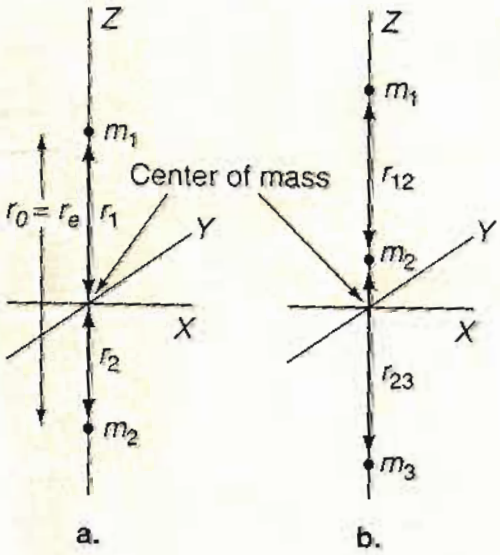


FIGURE 13.10
(a) A diatomic molecule. (b) A linear triatomic molecule.

The moment of inertia of a diatomic molecu
(see Figure 13.10a). The moment of inertia abo
axis) is zero. The moments about any axes at rigl
are given by

$$I = m_1 r_1^2 + m_2$$

where r_1 and r_2 represent the distances of the
respectively, from the center of mass of the molec
the values of r_1 and r_2 are given by

$$r_1 = \frac{m_2}{m_1 + m_2} r_0 \qquad r_2 =$$

Substitution of these expressions into Eq. 13.54 g

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 =$$

$r_0 = r_e$: equilibrium bond length

any rotation axis $\perp z$, ~~thro~~ through center of mass: same I

if rotation axis not through center of ~~moves~~ mass it moves like a particle in a large box

distances of center of mass to m_1 and m_2:

$$r_1 = \frac{m_2}{m_1 + m_2} r_0 \qquad r_2 = \frac{m_1}{m_1 + m_2} r_0$$

$$\Rightarrow I = m_1 r_1^2 + m_2 r_2^2$$

$$= \left[\frac{m_1 m_2^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2}{(m_1 + m_2)^2} \right] r_0^2$$

reduced mass: $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

$$\Rightarrow I = \mu \left[\frac{m_2}{m_1 + m_2} + \frac{m_1}{m_1 + m_2} \right] r_0^2$$

$$= \mu \underbrace{\frac{m_2 + m_1}{m_1 + m_2}}_{1} r_0^2 = \mu r_0^2$$

<u>absorption</u> lower to higher energy state:

(final state) $J+1 \leftarrow J$ (initial state)

<u>Selection rule</u>: <u>only</u> transitions with $\Delta J = \pm 1$ are allowed

$\rightarrow$ $J+1 \leftarrow J$ $(\Delta J = +1)$ absorption

$J+1 \rightarrow J$ $(\Delta J = -1)$ emission

$$\Delta E\,(J+1 \leftarrow J) = E_{J+1} - E_J$$

$$= \left[(J+1)(J+2) - J(J+1)\right]\frac{\hbar^2}{2I}$$

$$= (J+1)\left[J+2-J\right]\frac{\hbar^2}{2I}$$

$$= (J+1)\frac{\hbar^2}{I} = (J+1)\frac{h^2}{4\pi^2 I}$$

$$= 2(J+1)\frac{h^2}{8\pi^2 I}$$

$$\nu_J = \frac{\Delta E}{h} = 2\,(J+1)\frac{h}{8\pi^2 I}$$

$$\bar{\nu}_J = \frac{\nu}{c} = 2(J+1)\frac{h}{8\pi^2 c I}$$

$\bar{\nu}_J = 2(J+1)\tilde{B}$ $\quad \tilde{B} = \frac{h}{8\pi^2 I c}$ rotational constant

$J+1 \leftarrow J$ equally spaced lines: spacing $2\tilde{B}$

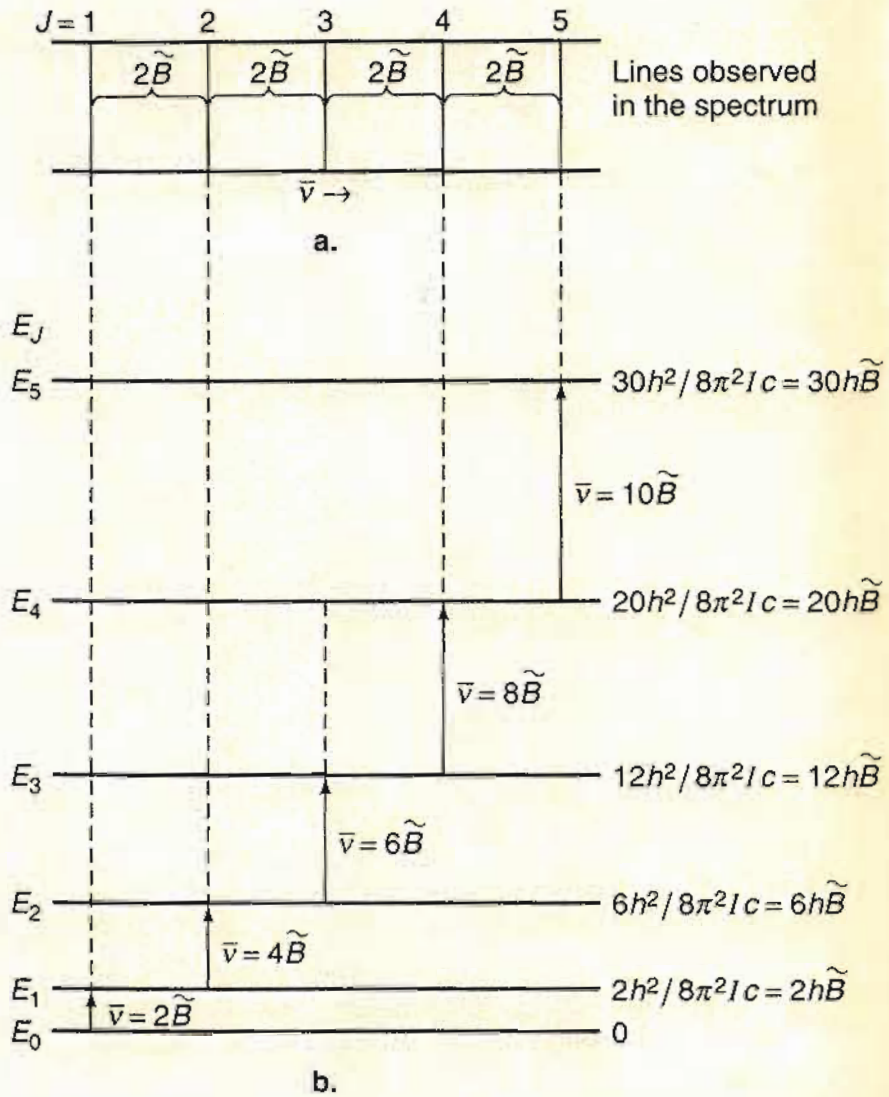


FIGURE 13.11
The constant $2\tilde{B}$ spacing of a pure rotational spectrum is shown in (a). The linearly increasing energy differences between the corresponding transitions are shown in (b).

EXAMPLE 13.7 Absorption by $H^{35}Cl$ occurs in the far inf
cm^{-1}, and the spacing between the neighboring lines is 20
moment of inertia and the internuclear distance in $H^{35}Cl$.

Solution From Eq. 13.62, with $J = 0$ (which gives the spac

$$\tilde{B} = \frac{\Delta\bar{\nu}}{2} = \frac{20.89\ (\text{cm}^{-1})}{2} = 10.445\ \text{cm}^{-1}$$

From Eq. 13.63 the moment of inertia is

$$I = \frac{h}{8\pi^2\tilde{B}c} = \frac{6.626 \times 10^{-34}(\text{J s})}{8\pi^2 \times 10.445\ (\text{cm}^{-1}) \times 2.998 \times 10^{1}}$$

$$= 2.680 \times 10^{-47}\ \text{kg m}^2$$

The reduced mass μ for a diatomic molecule is given by Eq. 1
atomic masses are given in Table 13.2.

$\tilde{B} = \frac{h}{8\pi^2 I c}$ rotational constant in cm^{-1}

$B = \tilde{B} c$ in Hz (s^{-1})

photon spin: $1\hbar$

$\Rightarrow$ absorption of a photon with spin $1\hbar$ <u>must</u> increase J by 1:

then angular momentum of the rotor increases by $1\hbar$

total angular momentum (rotor + photon) is conserved (unchanged)

measure line spacing in spectrum

$= 2\tilde{B}$

$\rightarrow I$ of the molecule

Absorption of $H^{35}Cl$ in FIR is near $200\ cm^{-1}$, line spacing $= 20.89\ cm^{-1}$

what is I and r_0 in $H^{35}Cl$?

line spacing $\Delta\tilde{\nu} = 2\tilde{B}$

$$\rightarrow \tilde{B} = \frac{\Delta\tilde{\nu}}{2}$$

$$\rightarrow \tilde{B} = \frac{20.89\ cm^{-1}}{2} = 10.445\ cm^{-1}$$

$$\tilde{B} = \frac{h}{8\pi^2 Ic} \Rightarrow I = \frac{h}{\tilde{B}\, 8\pi^2 c} = 2.680 \cdot 10^{-47}\ kg\, m^2$$

$$cm^{-1} \Rightarrow \frac{cm}{s}$$

$M_r(^{35}Cl)$: molar mass of ^{35}Cl
or relative mass

$$\mu = \frac{M_r(^{35}Cl)\, M_r(H)}{M_r(^{35}Cl) + M_r(H)} \cdot \frac{1}{N_A}$$

from mass of ^{35}Cl

$= 1.627 \cdot 10^{-24}\ g$

$= 1.627 \cdot 10^{-27}\ kg$

better accuracy possible!

$$I = \mu r_0^2, \quad r_0 = \sqrt{\frac{I}{\mu}} = 1.283 \cdot 10^{-10}\ m$$

Such distances are known to still better accuracy.

Linear Triatomic Molecules

The moment of inertia of a linear triatomic molecule is given by

$$I = m_1 r_{12}^2 + m_3 r_{23}^2 - \frac{(m_1 r_{12} - m_3 r_{23})^2}{m} \tag{13.65}$$

where $m = m_1 + m_2 + m_3$ and the individual atomic masses and positions are shown in Figure 13.10b. There are now two distances, r_{12} and r_{23}, to determine and this may be done by studying two molecules that are isotopically different. For example, deuterium may be substituted for hydrogen in HCN, and the pure rotational spectra

TABLE 13.2 Relative Atomic Masses for Several Isotopes*

Isotope	Rel. Atomic Mass	% Natural Abundance
$^{1}_{1}H$	1.007 825 035(12)	99.985(1)
$^{2}_{1}H$	2.014 101 779(24)	0.015(1)
$^{3}_{1}H$	3.016 049 27(4)	–
$^{3}_{2}He$	3.016 029 31(4)	$1.38(3)\times 10^{-4}$
$^{4}_{2}He$	4.002 603 24(5)	99.999863(3)
$^{12}_{6}C$	12 exactly (by definition)	98.90(3)
$^{13}_{6}C$	13.003 354 826(17)	1.10(3)
$^{14}_{6}C$	14.003 241 982(27)	–
$^{14}_{7}N$	14.003 074 002(26)	99.634(9)
$^{15}_{7}N$	15.000 108 97(4)	0.366(9)
$^{16}_{8}O$	15.994 914 63(5)	99.762(15)
$^{17}_{8}O$	16.999 131 2(4)	0.038(3)
$^{18}_{8}O$	17.999 160 3(9)	0.200(12)
$^{35}_{17}Cl$	34.968 852 721(69)	75.77(7)
$^{35}_{17}Cl$	36.965 902 62(11)	24.23(7)
$^{79}_{35}Br$	78.918 336 1(26)	50.69(7)
$^{81}_{35}Br$	80.916 289(6)	49.31(7)
$^{127}_{53}I$	126.904 473(5)	100

*The data are from "Isotopic composition of the elements, 1989," *Pure and Applied Chemistry*, **63**, 991–1002 (1991). They are the recommendations of the IUPAC Commission on Atomic Weights and Atomic Abundances. The numbers in parentheses are the uncertainties relating to the last digits quoted.

Table in book:

$M_r(^1H) = 1.007825035$ amu

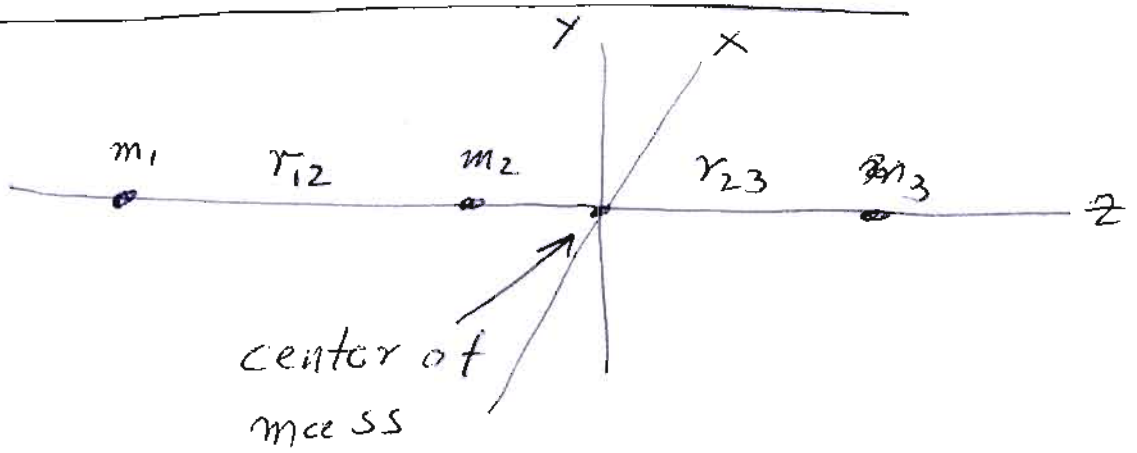
atomic mass unit

keep number

replace amu by g/mol

$M_r(^{35}Cl) = 34.968852721$ g/mol

linear triatomic molecule



$$I = m_1 r_{12}^2 + m_3 r_{23}^2 - \frac{(m_1 r_{12} - m_3 r_{23})^2}{m}$$

$$m = m_1 + m_2 + m_3$$

I around axis ⊥ to molecular axis (z) and through the center of mass (e.g. x or y)

→ determination of r_{12} and r_{23} should be possible

<u>by</u> use of 2 molecules with different isotopes (same atoms, same chemistry, different masses)

e.g. HCN, DCN

mass # → $^{1}_{1}H$ → HCN, $^{2}_{1}H$ → DCN

proton #

works <u>good</u> only when the bond lengths H–C and D–C are the same

in most atoms that works very well!

H → D errors ≈ 0.0005 nm in r

<u>Example</u>: $\tilde{B}(HCN) = 1.48\ cm^{-1}$

→ $B(HCN) = 4.431 \cdot 10^{10}\ s^{-1}$

$\tilde{B}(DCN) = \cancel{3.624 \cdot 10^{10}\ s^{-1}}\ 1.209\ cm^{-1}$

$B(DCN) = 3.624 \cdot 10^{10}\ s^{-1}$

$B = \tilde{B} \cdot c$

R H(D) − C and C ≡ N ?

$$I = \frac{h}{8\pi^2 \tilde{B} c} = \frac{h}{8\pi^2 B}$$

$$\rightarrow I(HCN) = 1.89 \cdot 10^{-46}\ kg\,m^2$$

$$I(DCN) = 2.32 \cdot 10^{-46}\ kg\,m^2$$

$$I(HCN) = m_H r_{CH}^2 + m_N r_{CN}^2 - \frac{(m_H r_{CH} - m_N r_{CN})^2}{m_H + m_C + m_N}$$

$$\|$$

$$I(DCN) = m_D r_{CD}^2 + m_N r_{CN}^2 - \frac{(m_D r_{CD} - m_N r_{CN})^2}{m_D + m_C + m_N}$$

<u>solution</u> (2 equations, 2 unknowns)

$$r_{CH} = r_{CD} = 0.106\ nm$$

$$r_{CN} = 0.116\ nm$$

$$I_{HCN} \cdot M_H = M m_H r_{CH}^2 + M m_N r_{CN}^2 - m_H^2 r_{CH}^2 + 2 m_H m_N r_{CH} r_{CN} - m_N^2 r_{CN}^2$$

$$I_{DCN} \cdot M_D = M_D m_D r_{CH}^2 + M_D m_N r_{CN}^2 - m_D^2 r_{CH}^2 + 2 m_D m_N r_{CH} r_{CN} - m_N^2 r_{CN}^2$$

$$I_{DCN} M_D = (M_D m_D - m_D^2) r_{CH}^2 + (m_N M_D - m_N^2) r_{CN}^2 + 2 m_D m_N r_{CH} r_{CN}$$

$$I_{HCN} M_H = (M_H m_H - m_H^2) r_{CH}^2 + (m_N M_H - m_N^2) r_{CN}^2 + 2 m_H m_N r_{CH} r_{CN}$$

$$= (m_C + m_N) m_H r_{CH}^2 + (m_C + m_H) m_N r_{CN}^2 + 2 m_H m_N r_{CH} r_{CN}$$

$$I_{DCN} M_D = (m_C + m_N) m_D r_{CH}^2 + (m_C + m_D) m_N r_{CN}^2 + 2 m_D m_N r_{CH} r_{CN}$$

$M_H = m_H + m_C + m_N \quad M_D = m_D + m_C + m_N$ 26 - 12

$$I_{HCN} = m_H r_{CH}^2 + m_N r_{CN}^2 - \frac{1}{M_H}(m_H r_{CH} - m_N r_{CN})^2$$

$$I_{DCN} = m_D r_{CH}^2 + m_N r_{CN}^2 - \frac{1}{M_D}(m_D r_{CH} - m_N r_{CN})^2$$

$$I_H = I_{HCN}, \quad I_D = I_{DCN}, \quad y = r_{CH}, \quad x = r_{CN}$$

$$M_H I_H = M_H m_H y^2 + M_H m_N x^2 - m_H^2 y^2 + 2 m_H m_N xy - m_N^2 x^2$$

$$M_D I_D = M_D m_D y^2 + M_D m_N x^2 - m_D^2 y^2 + 2 m_D m_N xy - m_N^2 x^2$$

$$M_H I_H = (M_H m_H - m_H^2) y^2 + (M_H m_N - m_N^2) x^2 + 2 m_H m_N xy$$

$$M_D I_D = (M_D m_D - m_D^2) y^2 + (M_D m_N - m_N^2) x^2 + 2 m_D m_N xy$$

$$M_H m_H - m_H^2 = (m_H + m_C + m_N) m_H - m_H^2$$

$$= m_H^2 + (m_C + m_N) m_H - m_H^2$$

$$= (m_C + m_N) m_H$$

$$M_D m_D - m_D^2 = (m_C + m_N) m_D$$

$$M_H m_N - m_N^2 = (m_H + m_C) m_N$$

$$M_D m_N - m_N^2 = (m_D + m_C) m_N$$

$$M_H I_H = (m_C + m_N) m_H y^2 + (m_H + m_C) m_N x^2 + 2 m_H m_N xy$$

$$M_D I_D = (m_C + m_N) m_D y^2 + (m_D + m_C) m_N x^2 + 2 m_D m_N xy$$

$$\frac{M_H I_H}{m_H} = \underbrace{(m_c + m_N) y^2}_{\parallel} + (m_H + m_c)\frac{m_N}{m_H} x^2 + \underbrace{2 m_N x y}_{\parallel} \quad (1)$$

$$\frac{M_D I_D}{m_D} = \overbrace{(m_c + m_N) y^2} + (m_D + m_c)\frac{m_N}{m_D} x^2 + \overbrace{2 m_N x y} \quad (2)$$

26 - 13

(1) − (2):

$$A = \frac{M_H I_H}{m_H} - \frac{M_D I_D}{m_D} = (5.103 - 3.248) \cdot 10^{-45}\ kg\, m^2$$
$$= 1.855 \cdot 10^{-45}\ kg\, m^2$$

$$B = \frac{m_H + m_c}{m_H} m_N - \frac{m_D + m_c}{m_D} m_N = (2.790 - 1.627) \cdot 10^{-22}\ kg$$
$$= 1.163 \cdot 10^{-22}\ kg$$

$$A = B x^2 \qquad \boxed{x = r_{CN} = (\pm) \sqrt{\frac{A}{B}}}$$

into (1):

$$\frac{M_H I_H}{m_H} = (m_c + m_N) y^2 + (m_H + m_c)\frac{m_N}{m_H}\frac{A}{B} + 2 m_N \sqrt{\frac{A}{B}}\, y$$

$$(m_c + m_N) y^2 + 2 m_N \sqrt{\frac{A}{B}}\, y + \left(\frac{m_H + m_c}{m_H}\right) m_N \frac{A}{B} - \frac{M_H I_H}{m_H} = 0$$

divide by $(m_c + m_N)$

$$C = 2 \frac{m_N}{m_c + m_N} \sqrt{\frac{A}{B}}$$

$$D = \frac{m_H + m_c}{m_c + m_N} \frac{m_N}{m_H} \frac{A}{B} - \frac{M_H I_H}{m_H (m_c + m_N)}$$

$$y^2 + Cy + D = 0$$

$$\boxed{y_{1,2} = (r_{CH})_{1,2} = \frac{1}{2}\left(-C \pm \sqrt{C^2 - 4D}\right)}$$

26 -14

choose the better value:

1) positive

2) that one closer to 0.1 nm

Moments of Inertia

General

~~co~~ center of mass $\underline{R}$:

$$\underline{R} = \frac{\sum_i m_i \underline{r}_i}{\sum_i m_i}$$

i runs over all atoms

m_i: mass of atom i
(not molar mass)

$\underline{r}_i$: coordinate vector from the origion
$(x = y = z = 0)$ to ~~mass~~ atom ~~i~~ i

moment of inertia

$$I = \sum_i m_i d_i$$

d_i: distance from atom i to the rotation axis

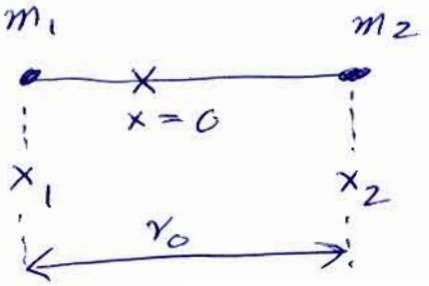
different for each axis!

Diatomics

x : center of mass at $x=0$

atoms at x_1 and x_2 on x-axis

<u>important</u> : $x_1 < 0$, $x_2 > 0$



$r_0 = x_2 - x_1$

because $x_1 < 0$

$$\rightarrow x_2 = r_0 + x_1$$

center of mass:

$$\frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} = 0$$

$$\rightarrow m_1 x_1 + m_2 x_2 = 0$$

$$m_1 x_1 + m_2 (r_0 + x_1) = 0$$

$$(m_1 + m_2) x_1 = -m_2 r_0$$

$$x_1 = -\frac{m_2}{m_1 + m_2} r_0 < 0$$

$$x_2 = r_0 + x_1 = r_0 - \frac{m_2}{m_1 + m_2} r_0$$

$$= \frac{m_1 + m_2 - m_2}{m_1 + m_2} r_0 = \frac{m_1}{m_1 + m_2} r_0$$

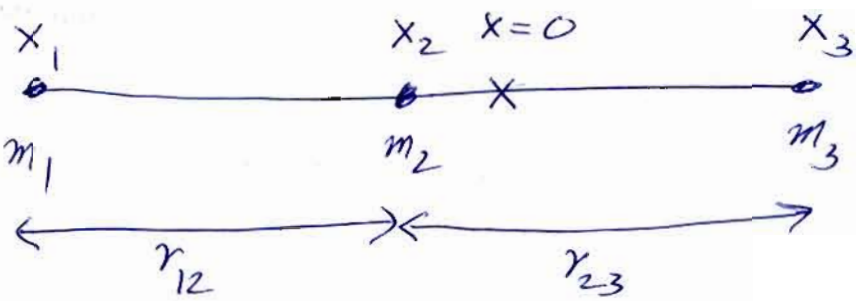
distances

$$d_1 = r_1 = |x_1| = \frac{m_2}{m_1 + m_2} r_0$$

$$d_2 = r_2 = |x_2| = \frac{m_1}{m_1 + m_2}$$

for moment of inertia from here see notes

Linear Triatomis



center of mass $\dfrac{m_1 x_1 + m_2 x_2 + m_3 x_3}{m_1 + m_2 + m_3} = 0$

$$\rightarrow \quad m_1 x_1 + m_2 x_2 + m_3 x_3 = 0$$

$$r_{12} = x_2 - x_1 \qquad r_{12} + r_{23} = x_3 - x_1$$

$$r_{23} = x_3 - x_2 \qquad x_1 = x_3 - (r_{12} + r_{23})$$

$$x_2 = x_3 - r_{23}$$

$$m_3 x_3 = - m_1 x_1 - m_2 x_2$$

$$= - m_1 (x_3 - r_{12} - r_{23}) - m_2 (x_3 - r_{23})$$

$$\underbrace{(m_1 + m_2 + m_3)}_{m} x_3 = m_1 (r_{12} + r_{23}) + m_2 r_{23}$$

$$x_3 = \frac{m_1}{m} (r_{12} + r_{23}) + \frac{m_2}{m} r_{23}$$

$$x_2 = x_3 - r_{23}$$

$$= \frac{m_1}{m} (r_{12} + r_{23}) + \left(\frac{m_2}{m} - 1\right) r_{23}$$

$$x_1 = x_3 - (r_{12} + r_{23})$$

$$= \left(\frac{m_1}{m} - 1\right)(r_{12} + r_{23}) + \frac{m_2}{m} r_{23}$$

to get I x_1, x_2, and x_3 in terms of r_{12} and r_{23} must be inserted into

$$I = m_1 x_1^2 + m_2 x_2^2 + m_3 x_3^2$$

and gives after a massy calculation the result. Don't try that. Such formulas are tabulated!

Obj : – rotations
– vibrations (beginning)

Microwave Spectroscopy

$H^{35}Cl$: $I = 2.680 \cdot 10^{-47}\ kg\,m^2$, $\tilde{B} = 10.445\ cm^{-1}$

$\rightarrow \tilde{\nu} = 20.89\ cm^{-1}$, $41.78\ cm^{-1}$, ...

IR spectroscopy : infrared light is passed through the sample cell

then onto a diffraction grating

then into a heat sensitive detector

different directions, different $\tilde{\nu}$

larger molecules e.g. $^{16}O\ ^{12}C\ ^{32}S$

$I = 1.38 \cdot 10^{-45}\ kg\,m^2$ (larger), $\tilde{B} = 0.203\ cm^{-1}$

$\tilde{\nu} = 0.406\ cm^{-1}$, $0.812\ cm^{-1}$, ...

with such small and close $\tilde{\nu}$ values normal IR measurement with a diffraction grating impossible

microwaves!

Klystron

electronically controlled oscillator

→ monochromatic (narrow band of $\bar{\nu}$ values)

→ into metal wave guide

in there ~~metal~~ mica cell at 0.01–0.1 torr pressure

containing the sample

at higher pressures:

line broadening by collisions

→ continous spectrum (useless)

detection by metal antenna

coupled to an oscilloscope

→ $\bar{\nu}$ to more than 7 significant figures

h is <u>now</u> known to 8 figures

→ accurate r_e values

$\Delta E_J \approx 5 \cdot 10^{-22}$ J/mol $\approx k_B T$ at room-T

→ rotational levels excited at room-T

→ transition <u>not</u> from J=0 (from excited)

large molecules

overlap of the rotational spectra from different vibrational states

in microwave usually not $\bar{\nu}$ used but ν in MHz or GHz (up to some 100 GHz)

Nonlinear molecules

∞ no. of axis through center of mass

→ ~~fro~~ for each rotation axis α there is a moment of inertia, I_α

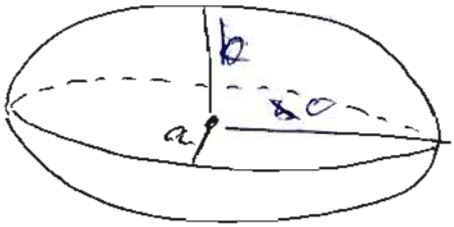
$$I_\alpha = \sum_i m_i R_{i\alpha}^2$$

m_i: mass atom i

$R_{i\alpha}$: distance atom i to axis α

from center of mass draw a line along all the rotation axis α of length $1/\sqrt{I_\alpha}$

→ ellipsoid of inertia



3 principal axis of an ellipsoid

I_a, I_b, I_c

large I ~ small length in ellipsoid
($1/\sqrt{I}$)

largest I : largest rotation axis
of a molecule with C_x
symmetry. Principal
C_x axis with largest x
that is rotation axis with to
largest I
with any orientation of x, y, z
through center of mass such can
ellipsoid can be determined.
usually rotated
and principal axis of the ellipsoid
define the principal rotation axis

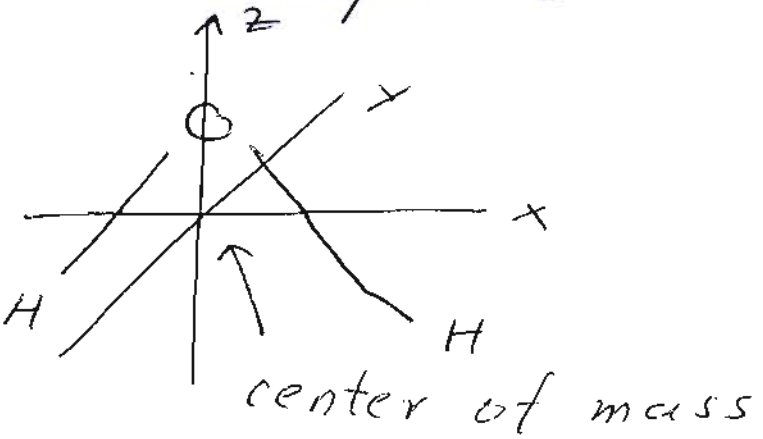
direction of symmetry axis ~~w~~ C_x with largest x is the principal axis with largest I

any reflection plane σ_h must contain 2 of the principal axis

<u>type</u>

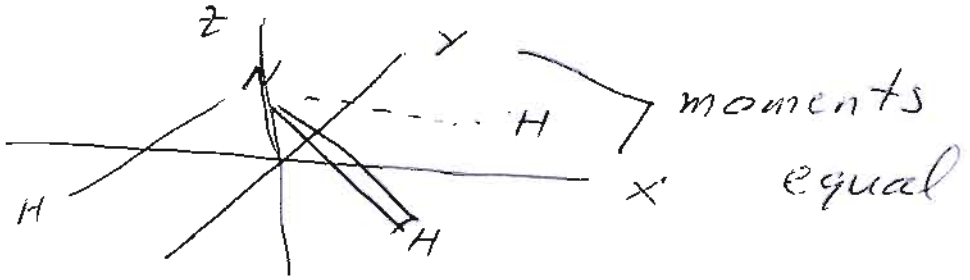
<u>asymmetric top</u>

3 <u>different</u> principal moments of inertia : example H_2O



<u>Symmetric top</u>

2 of the 3 principal moments of inertia are equal : NH_3



<u>prolate top</u>

the larger 2 are equal

cigar shaped ellipsoid (2 small axis)

<u>oblate top</u>

the smaller 2 are equal (2 large axis)

pancake shaped ellipsoid

<u>spherical top</u>

all 3 moments are equal

$I_a = I_b = I_c$, CH_4

<u>Stark effect</u>

$\Delta\tilde{\nu}$ can be so small, that one cannot decide to which J a line belongs:

even $J=1 \leftarrow J=0$ may be not present

dipole moment $\rightarrow$ interaction with a static E-field

$\rightarrow$ $2J+1$ levels belonging to J will split into $2J+1$ levels with different energies

→ multiplet structures in Stark effect allow to assign $J+1 \leftarrow J$ to each rotational line

<u>also</u> dipole moment can be obtained from level splittings

Vibrational - Rotational Spectra

IR region → vib. + rot. transitions occur together

→ series of bands:
groups of rotational lines for each vibrational transition

bands in <u>gas phase</u> samples:
sharp lines because of free rotations

<u>liquids, solids</u>: broad bands, rot. lines not resolved, because no free rotations

aqueous solutions

not possible:

1) usually KBr cells

2) strong H_2O absorptions in IR

dispersion of samples usually in KBr or others
↳ no IR absorption

→ mix sample with KBr
+ press a transparent disk

Diatomic molecules simplest gas-phase spectra

harmonic oscillator: $E_v = (v + \frac{1}{2}) h\nu_0$

v: vibrational quantum no. 0, 1, 2, ---
ν_0: fundamental frequency
k: force constant

displacement of masses such that center of mass does not move
$x = x_1 + x_2$: change of bond length from r_e

J. Stark received the Nobel prize in physics in 1919 for discovering the Stark effect in 1913.

German physicist Johannes Stark (1874-
$2J + 1$ degenerate rotational energy leve
structure is observed for all lines with
to particular observed spectral lines, sin
not be the one for $J = 0$. Since the n
unambiguous assignments can be made.

A second advantage of the Stark ef
found because the absorption line shift i
field and on the dipole moment.

13.4 VIBRATIONAL-ROTATIONAL SPECTRA OF MO

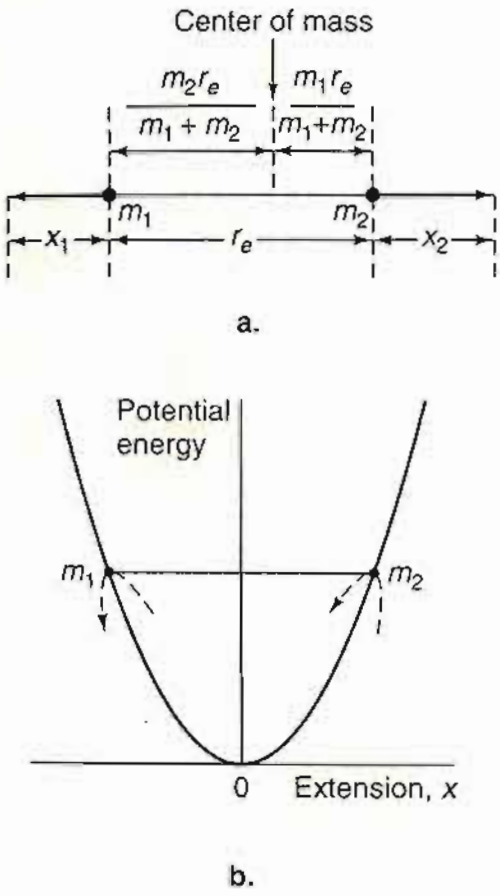


FIGURE 13.13
(a) The displacements of the masses m_1 and m_2 during the vibration of a diatomic molecule. (b) The potential-energy curve (a parabola) for a harmonic oscillator.

The spectra observed in the infrared re
nied by rotational transitions. Infrared
band corresponding to changes in the v
in the band corresponding to a superim

The infrared bands obtained with
sharp lines, since the molecules can
liquid phase or in solution, however,
bands are blurred. It is not possible to
in aqueous solution, since water abs
masks the spectrum of the solute. M
made with the substance in the gas p
common modern technique is to dis
usually potassium bromide. The samp
which is then pressed into a transpa
supported in the beam of the infrared

Diatomic Molecul

The simplest infrared spectra are thos
studied in the gas pha In Section 1
harmonic oscillator, a the energy (E

$$E_v =$$

where v is the *vibrational quantum*
related to the *force constant* k in the
m_1 and m_2 connected by a spring.
the distance betwee the masse w
is at distances

$$\frac{m_2}{m_1 + m_2}$$

from the masses m_1 and m_2. Suppose
masses are displaced by distances x_1

enter of mass : no change

$$\Rightarrow \quad x_1 = \frac{m_2}{m_1 + m_2} x \qquad x_2 = \frac{m_1}{m_1 + m_2} x$$

$x = x_1 + x_2$: change of bond length around r_e

$$\rightarrow \mu \ddot{x} = -kx$$

$\ddot{x}$ means $\frac{d^2 x}{dt^2}$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

reduced mass

$F = -kx$ restoring force

$$F = -\frac{dE_p}{dx}$$

$$\rightarrow E_p = \frac{1}{2} k x^2 \qquad \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$k = 4\pi^2 \nu_0^2 \mu$$

solution $x(t) = A \cos(2\pi \nu_0 t)$

turning point:

maximum E_p, no E_k

equilibrium: maximum E_k, no E_p

between: mixed, but $E_t = E_k + E_p = \text{const.}$

<u>real shape</u>:

near minimum: parabola good

Large x: bond breaks

$\Rightarrow E_p = 0$: free atoms

Small x: positive nuclei come close together: $E_p \to +\infty$

$\to$ levels no more equally spaced but are more dense at higher E_v

<u>harmonic</u>: starting point

<u>after</u>: corrections for anharmonicity

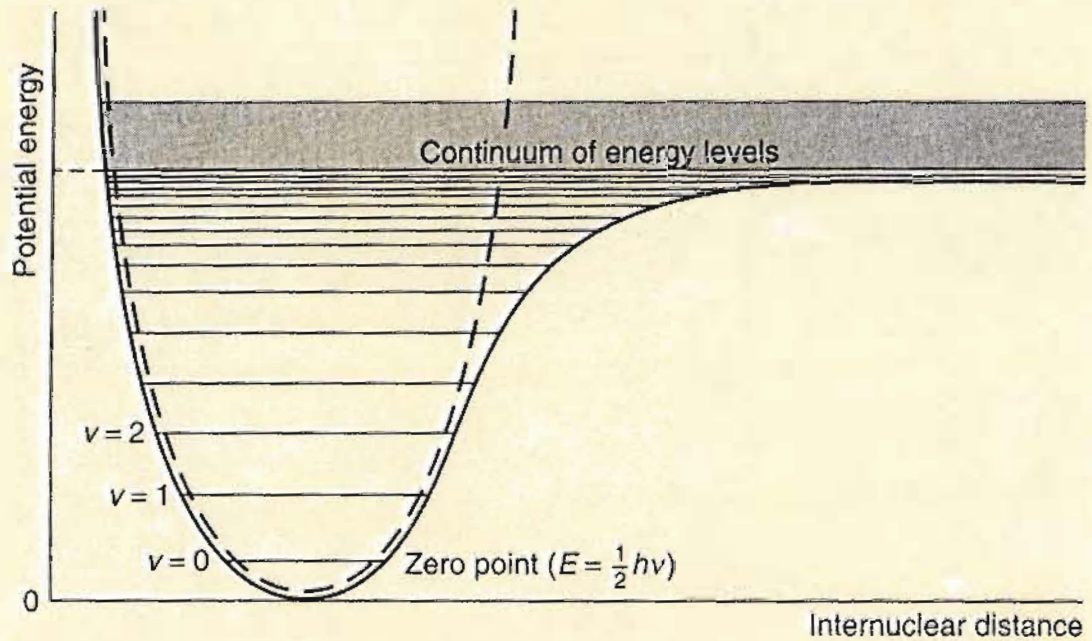


FIGURE 13.14
The actual potential-energy curve for a diatomic molecule (solid curve) with a parabola imposed on it (dashed line). The lowest horizontal lines, representing the quantized vibrational energy levels, are approximately equally spaced. However, as the curve deviates from the parabola, the levels become closer together.

spectrum with rotational changes superimposed. The situation is represented schematically in Figure 13.15 which shows two vibrational states corresponding to $v = 0$ and $v = 1$. The rotational quantum numbers in the $v = 0$ state are designated J'' and those in the $v = 1$ state are J'. To the extent that the behavior is harmonic, the average internuclear distance is r_e for all vibrational states, so that the rotational constant B may be assumed to be the same for all values of v and J.

For strict harmonic motion the selection rules for vibrational-rotational transitions are usually

$$\Delta v = \pm 1 \quad \text{and} \quad \Delta J = \pm 1 \tag{13.87}$$

In other words, the vibrational state can only change to a neighboring one, and at

Obj Vibration - Rotation spectra

Born - Oppenheimer approximation:

$$E = E_v + E_J \quad \text{possible}$$

$B = \frac{h}{8\pi^2 I}$ rotational constant in $Hz = s^{-1}$

$c\tilde{B} = B \quad \tilde{B}$: in cm^{-1}

$$E_J = J(J+1)\frac{h^2}{8\pi^2 I} = J(J+1)Bh$$

$$E_{v,J} = (v+\tfrac{1}{2})h\nu_0 + J(J+1)Bh$$

transition with $\Delta v = 0$:

pure rotational spectrum

all others: $\Delta v = \pm 1$ (harmonic)

rotation excitations in each

involved vibrational level

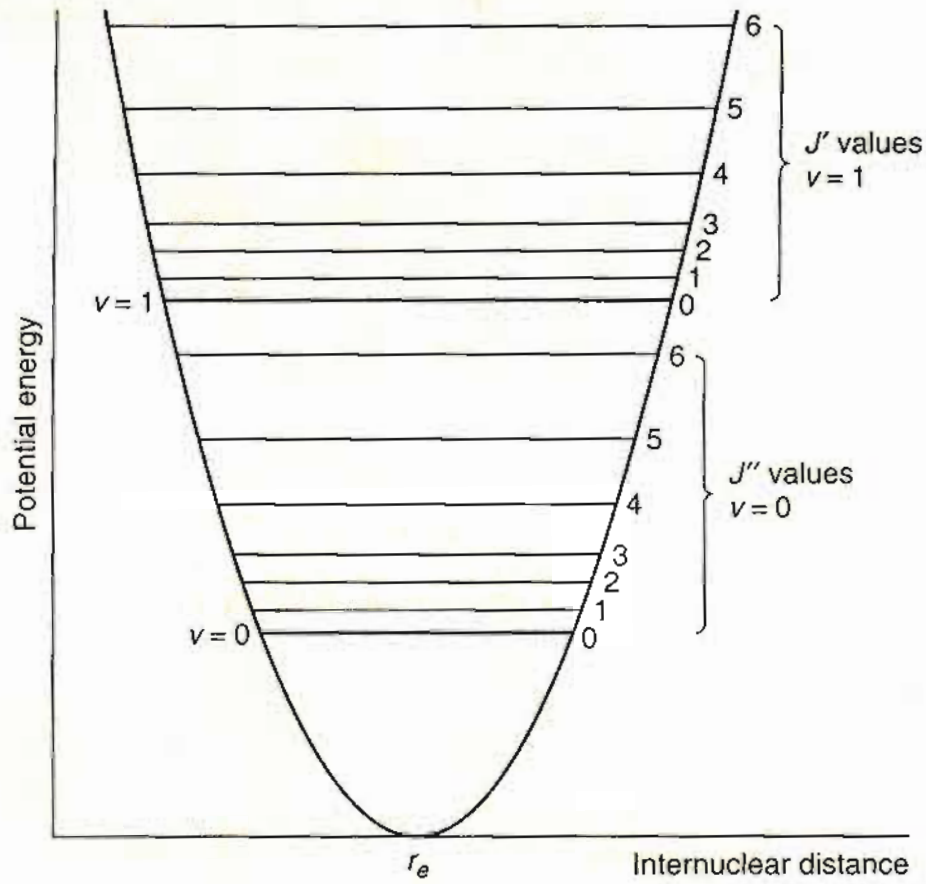


FIGURE 13.15
A potential-energy curve, showing the two lowest vibrational states ($v = 0$ and $v = 1$) with rotational states superimposed.

If $v' - v'' = \cancel{0}$, 1

$$\Delta T_{v,J} = \tilde{\nu}_0 + \tilde{B}[J'(J'+1) - J''(J''+1)] \tag{13.92}$$

Associated with this change of $\tilde{\nu}$ there are two allowed changes of J. If $J' = J'' + 1$, the allowed wavenumbers are given by

$v = 0 : J''$, $v = 1$ J'

if harmonic behaviour:

r_e same for all v

$\rightarrow$ B same for all v

<u>harmonic</u> selection rules for vib.-rot. (vibrational-rotational) transitions:

$$\Delta v = \pm 1 \quad , \Delta J = \pm 1$$

vib. transition <u>only</u> the neighboring vib. state and <u>only</u> together with a rotational change by $\Delta J = 1$

$$\Rightarrow \Delta E_{v''J'' \leftarrow v'J'} = \underset{\text{higher}}{E_{v'J'}} - \underset{\text{lower}}{E_{v''J''}}$$

$$= (v' - v'')h\nu_0 + \left[J'(J'+1) - J''(J''+1)\right]\tilde{B}hc$$

$\frac{\Delta E}{h\nu} \rightarrow$ lines in cm^{-1} (wavenumbers)

spectroscopic term: $T = \frac{E}{hc}$

electronic term: T_e , vib. term: G

rot. term: F

line: term difference,

indices: the ~~low~~ higher ones v', J'

$$\Delta T_{v'J'} = (v'-v'')\tilde{\nu}_0 + [J'(J'+1) - J''(J''+1)]\tilde{B}$$

$$\tilde{\nu}_0 = \frac{\nu_0}{c} \qquad B = \frac{h}{8\pi^2 I} \qquad \tilde{B} = \frac{B}{c}$$

selection rule: $\Delta v = v' - v'' = +1$

(absorption!)

$$\Delta T_{v'J'} = \tilde{\nu}_0 + [J'(J'+1) - J''(J''+1)]\tilde{B}$$

vibrational levels are at higher energy than the rotational ones

→ at room-temperature only $v=0$ occupied by molecules

→ in absorption only $v''=0 \to v'=1$ transitions occur

rotational levels are at much lower energies: many occupied at room temp.

⇒ for J'' (lower) to J' higher (absorption) $\Delta J = \pm 1$ possible

J' is in $v=1$, J'' in $v=0$ → all J' higher than all J''

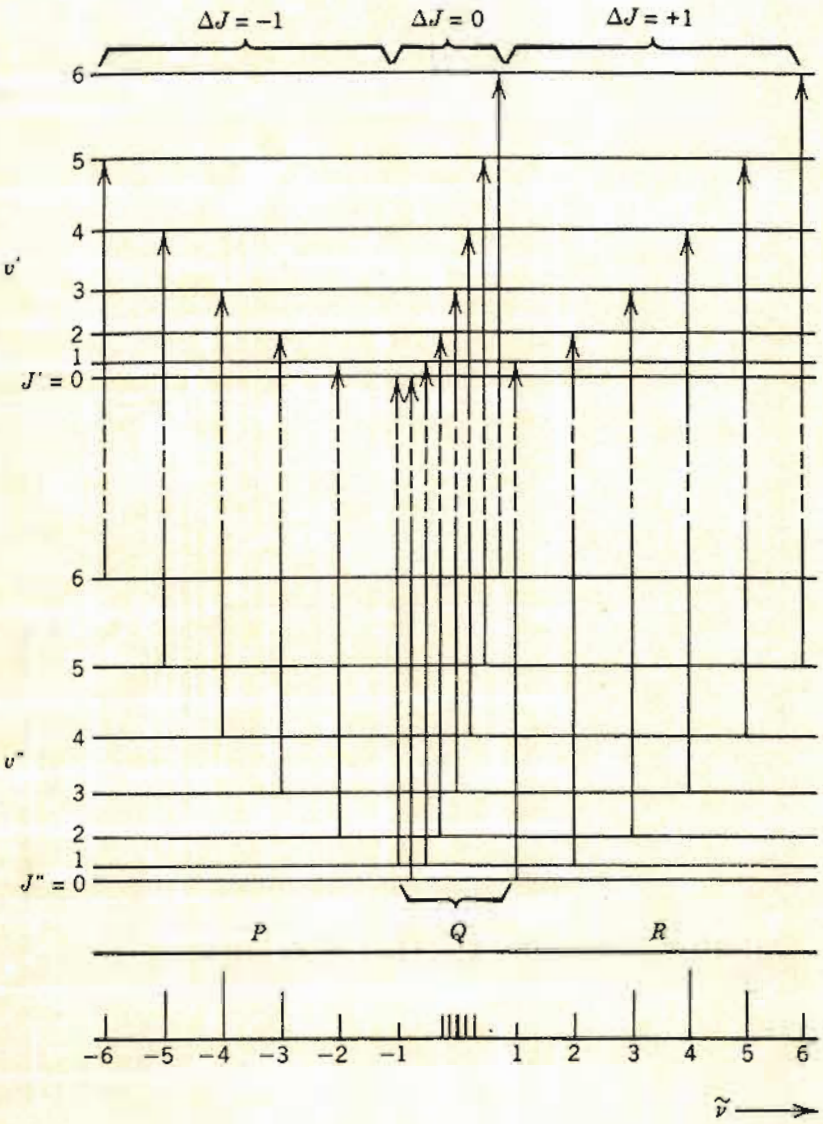


Figure 14.7 Vibrational and rotational energy levels for a diatomic molecule and the transitions observed in the vibration–rotation spectrum when the transition between v' and v'' is allowed. In the spectrum shown at the bottom the lines are indexed with their m values. The relative heights of the spectral lines indicate relative intensities of absorption.

which expresses the energy of a level as the sum of the first term of the rotational term value (equation 14.31) and the first two terms of the vibrational term value (equation 14.63). Now it is necessary to put a subscript v on B_v since the rotational constant depends on the vibrational quantum number v.

The wavenumber of the line resulting from the transition $(v'', J'' \rightarrow v', J')$ is given by

$\underline{J' = J'' + 1}$: $\Delta J = +1$

$\tilde{\nu} = \tilde{\nu}_0 + 2(J''+1)\tilde{B}$ ← lower v

series of lines above $\tilde{\nu}_0$

→ <u>R-branch</u>

$$[J'(J'+1) - J''(J''+1)] = [(J''+1)(J''+2) - J''(J''+1)]$$

$$= (J''+1)[J''+2-J'']$$

$$= 2(J''+1)$$

$\underline{J' = J''-1}$: $\Delta J = -1$

$$\tilde{\nu} = \tilde{\nu}_0 - 2J''\tilde{B}$$

series of lines below $\tilde{\nu}_0$

→ <u>P-branch</u>

$K = \cancel{0}, \pm 1, \pm 2, \cdots$ <u>combined counter</u>

P-branch : $\underline{K = -J''} = -1, -2, \ldots$ $\Delta J = -1$ → $J'' = J' + 1 = 1, 2, \cdots$

R-branch : $\underline{K = J''+1} = (0), 1, 2, \cdots$ $\Delta J = +1$ $J'' = J' - 1$ $\cancel{= 0, 1, 2,}$ $= -1, 0, 1, 2, \ldots$

J' starts with $\cancel{0}$ 1 ⇒

<u>some cases</u> : $\Delta J = 0$ possible

→ $\tilde{\nu}_0$ line : Q branch

in most cases for bicdlen

pure vib. line ($\tilde{\nu}_0$) does not occur

remember: HCl spectrum

gap at $\Delta J = 0$

rotational lines are all

splitted in 2:

isotopes: $H^{35}Cl$, $H^{37}Cl$

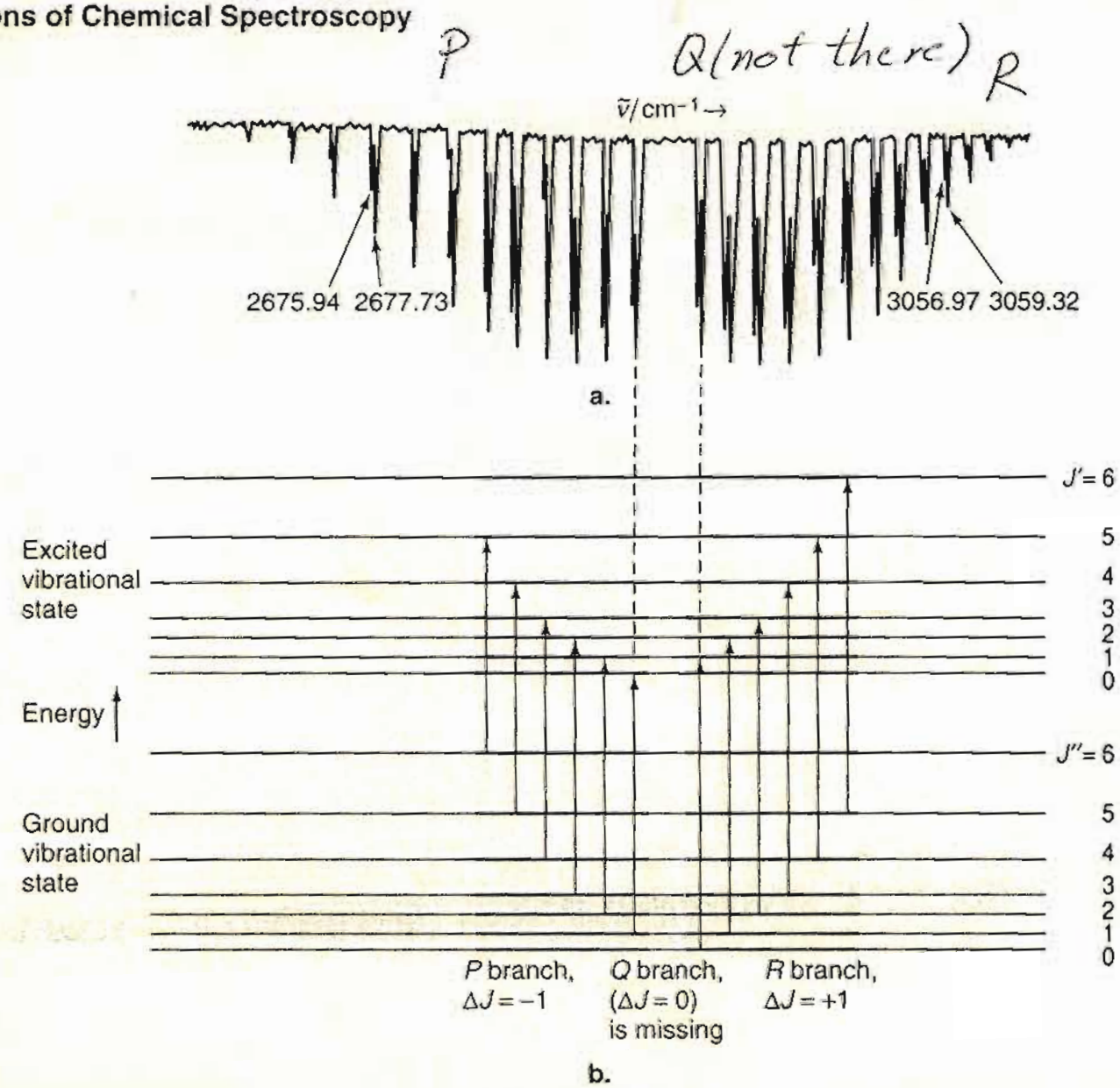
almost ~~50~~ 75 : ~~50~~ 25 abundancies

line spacing in R or P branch:

$2\tilde{B} \rightarrow I \rightarrow r_e$

position of band center:

$\tilde{\nu}_0 \rightarrow k$ force constant



.16
rational-rotational spec-
l, showing the P- and
. The absorption band is
er high resolution where
of the lines is due to
e of the two isotopes
Cl. There is a missing
een the two bands
$J = 0$ is forbidden. (b)
evels corresponding to
nal states, $v = 0$ and
ing the transitions that
he P- and R-branches.

Deviations from the simple type of behavior that we have just described arise because of the **anharmonicity** of molecular vibrations. If a potential-energy curve

Anharmonicity

deviation from simple harmonic behavior

e.g.: bond breaking is possible!
(anharmonic effect)

also quantized vibrational levels become more and more dense the closer E_v comes to 0 (bond breaking), the higher v is

bond broken: free atoms:

continuum of levels like a particle in a very large box (level spacing almost 0)

anharmonic vibrations:

additional bands ($\Delta v = 1$ does not hold), other selection rules

to take that into account:

power series expansion of the terms $G_v = \frac{E_v}{hc}$ in $(v+\frac{1}{2})$:

$$G_v = \omega_0 \left[(v+\tfrac{1}{2}) - x_e (v+\tfrac{1}{2})^2 + y_e (v+\tfrac{1}{2})^3 - \cdots \right]$$

$\omega_0 = \tilde{\nu}_0$, x_e, y_e: anharmonicity constants

usually: x_e alone is enough:

$$G_v = \omega_0 \left[(v+\tfrac{1}{2}) - x_e (v_e+\tfrac{1}{2})^2 \right]$$

gives smaller level spacings (levels more dense) the larger v becomes as in experiment

$$G_v = \omega_0 \left[1 - x_e (v+\tfrac{1}{2}) \right] (v+\tfrac{1}{2})$$

zero-point energy (in cm^{-1}):

$$G_0 = \frac{1}{2} (1 - \tfrac{1}{2} x_e) \omega_0$$

~~usually~~ usually close to harmonic zero-point energy E_0

<u>because</u> typically: $x_e \approx 0.01$

anharmonic selection rules:

$$\Delta v = \pm 1, \pm 2, \pm 3$$

→ multiple level transitions (jumps) but with less intensity than the fundamental absorption, $\Delta v = +1$

at room-temp.: almost all molecules in E_0 (not all!)!

$$\Delta E_1 = E_1 - E_0 = h\nu_0 (1 - 2x_e)$$

fundamental absorption

$$\Delta E_2 = E_2 - E_0 = 2h\nu_0 (1 - 3x_e)$$

first overtone

$$\Delta E_3 = E_3 - E_0 = 3h\nu_0 (1 - 4x_e)$$

second overtone

⋮

→ higher $\tilde{\nu}$ (overtones) and reduced intensity

<u>all</u> with rotational fine structure ($\Delta J = \pm 1$)

$T > 500\,K$:

enough molecules occupy $v=1$ level

to see lines from $v=1$

$$\Delta E_{2\leftarrow 1} = E_2 - E_1 = h\nu_0 (1-4x_e)$$

1) lower frequency than fundamental
2) intensity increase when T increases

→ name: <u>hot bands</u>

<u>real molecules</u>

<u>not</u> $E_p = \frac{1}{2}kx^2$ (harmonic)

but <u>Morse potential</u>:

$$E_p = D_e (1 - e^{-ax})^2$$

D_e, a fitted to observed spectrum

D_e: classical dissociation energy

→ x_e, $\tilde{\nu}_0$ → D_0 quantum mech. dissociation energy $(D_e + \frac{1}{2}\tilde{\nu}_0)$

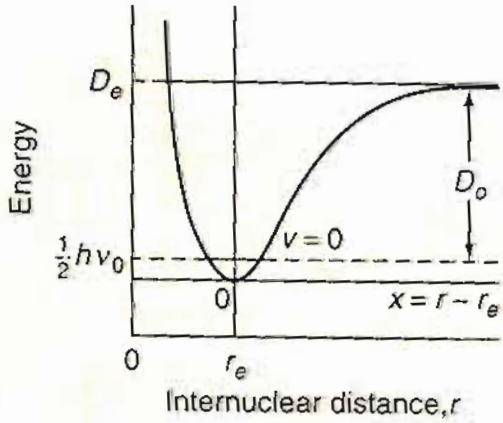


FIGURE 13.17
The potential-energy curve predicted by the Morse equation, Eq. 13.104.

Morse (b. 1903). This equation, known as the Mo

$$E_p = D_e(1 - e^{-ax}$$

where $x = r - r_e$ (i.e., the extension of the bon and D_e and a are constants. The curve represen Figure 13.17. When $x = 0$, $E_p = 0$; when x ap D_e. The quantity D_e is therefore the *classical* dis the experimental dissociation energy plus the zero the equation is that if the form of the potential-en spectroscopic data, the curve can be fitted to the M then known, and the dissociation energy D_0 can discussion see Example 13.10 and Section 13.6.

Normal Modes of Vibration

A diatomic molecule vibrates according to a simple tional frequency. The vibrational motions of molecu are a superposition of a number of basic vibration **vibration.** In order to bring out this concept, we wil a linear triatomic molecule.

The linear triatomic system is shown schemat treatment we will ignore bending vibrations and w along the axis of the molecule. The center of mass is moments are taken about the origin when the molec

Stretching Vibrations

$$m_1(r_{12} - y) = m_2 y + m_3($$

where y is the distance between the center of mass an are displaced to the right by the distances x_1, x_2, an

$$m_1(r_{12} - y - x_1) = m_2(y + x_2) + m_3($$

<u>Obj</u> repeat some rot.-vib.
polyatomic molecules
normal coordinates
group frequencies

$$\tilde{\nu} = \Delta T_{0,J} = \tilde{\nu}_0 + \tilde{B}\left[J'(J'+1) - J''(J''+1)\right]$$

lower — higher $v=1$ — lower $v=0$

<u>R-branch</u> $\Delta J = +1$: $J' = J''+1$

start with $J''=0$

$$\tilde{\nu} = \tilde{\nu}_0 + \tilde{B}\left[(J''+1)(J''+2) - J''(J''+1)\right]$$

$$= \tilde{\nu}_0 + \tilde{B}(J''+1)\left[J''+2-J''\right]$$

$$= \tilde{\nu}_0 + 2\tilde{B}(J''+1) = \tilde{\nu}_0 + 2\tilde{B}K$$

$K = 1\ (J''=0),\ 2\ (J''=1),\ 3\ (J''=2), \ldots$

in R: $K = J''+1$ $\quad J''=0,1,\ldots$

<u>P-branch</u> $\Delta J = -1$, $J' = J''-1$

$\Rightarrow$ start with $J''=1$ (then $J'=0$)

($J''=0$ would give $J'=-1$

which does <u>not</u> exist)

$$\tilde{\nu} = \tilde{\nu}_0 + \tilde{B}\left[(J''-1)J'' - J''(J''+1)\right]$$

$$= \tilde{\nu}_0 + \tilde{B}J''\left[J''-1-J''-1\right]$$

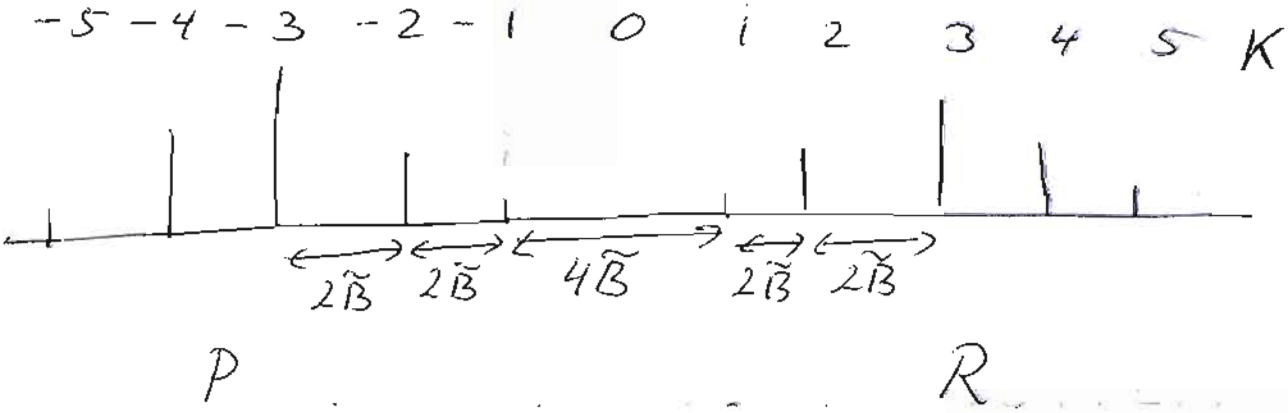
$$= \tilde{\nu}_0 - 2\tilde{B}J'' = \tilde{\nu}_0 + 2\tilde{B}K$$

$$K = -J''$$

$$\Rightarrow K = -1\ (J''=1),\ -2\ (J''=2),\ -3\ (J''=3), \ldots$$

→ spacing in <u>both</u> branches $2\tilde{B}$

<u>Q-branch</u> can be labelled with $K=0$



Q mostly forbidden, pure vibrat. $\tilde{\nu}_0$ does mostly not exist

relative intensities I

$$\frac{I_{J''}}{I_{J''=0}} \approx \frac{N_{J''}}{N_{J''=0}} = (2J''+1)\, e^{-\frac{hc\tilde{B}}{k_B T} J''(J''+1)}$$

because relative, almost equal

Normal modes of vibration

Taylor series of E_p around minimum

$$E_p = E_0 + \frac{1}{2}\sum_{ij} K_{ij} q_i q_j$$

i,j atom numbers

$$q_i = \sqrt{m_i}\, x_i$$

mass weighted cartesian coordinates

~~$E_0 = 0$~~ , ~~because~~ in ~~mini~~ a Taylor series, term linear in q_i is

$$\sum_i \left.\frac{\partial E_p}{\partial q_i}\right|_{q_i = q_i^m} \cdot q_i = 0$$

$\hookrightarrow$ 0 in energy minimum q_i^m

$$K_{ij} = \left.\frac{\partial^2 E_p}{\partial q_i \partial q_j}\right|_{\substack{q_i = q_i^m \\ q_j = q_j^m}}$$

put $E_0 = 0$ because E_p only important relative to minimum

problem: cross terms $q_i q_j$

→ combinations of the coordinates q_i such that for these linear combinations u_k, E_p is diagonal:

$$E_p = \frac{1}{2} \sum_k K_k u_k^2$$

normal coordinates
normal modes

complicated combinations of q-s and atomic masses in a molecule

→ normal vibrations (oscillations ~~around~~ along u_k), each 1 with frequency ν_k:

$$\nu_k = \frac{1}{2\pi} \sqrt{\frac{k_k}{\mu_k}}$$

reduced mass of normal mode k

k_k force constant of vibration k

general molecule with

N atoms: 3N cartesian coordinates

$K_k = 0$

→ 3 translations, 3 rotations

+ (3N−6) normal vibrations modes

<u>linear molecule</u> (3N−5) normal modes

example: normal modes of CO_2

linear: O=C=O

→ 3·3−5 = 9−5 = 4 normal modes

2 are degenerate (same frequency)

picture shows result.

Forget the overkill calculation

no translations, no rotations

center of masses conserved

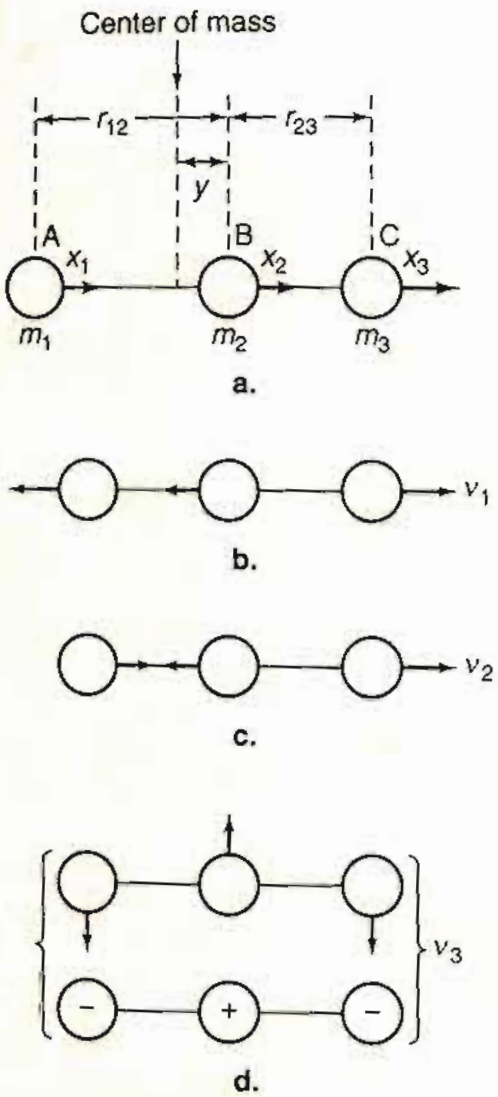


FIGURE 13.18
(a) Stretching vibrations of a linear triatomic molecule. (b) The symmetric stretching (breathing) vibration of a linear triatomic molecule. (c) The antisymmetric stretching vibration. (d) The two degenerate bending vibrations.

and

$$m_1 m_3 \ddot{x}_3 + k_{23}[m_1 x_1 + (m_2$$

To solve these equations, we look for solutions

$$x_1 = A_1 \cos 2\pi$$
$$x_3 = A_3 \cos 2\pi$$

with the same frequency ν for both displacemen

$$\ddot{x}_1 = -4\pi^2\nu^2 x_1 =$$
$$\ddot{x}_3 = -4\pi^2\nu^2 x_3 =$$

where λ has been written for $4\pi^2\nu^2$. Insertion
and 13.111 leads to two simultaneous equation

$$[-\lambda m_1 m_2 + k_{12}(m_1 + m_2)]$$
$$m_1 k_{23} x_1 + [-\lambda m_2 m_3 + k_{23}$$

Equations of this type are only consistent

$$\begin{vmatrix} -\lambda m_1 m_2 + k_{12}(m_1 + m_2) & \\ m_1 k_{23} & -\lambda m_2 m \end{vmatrix}$$

This determinental equation is a quadratic equ

$$\lambda^2 - \left(\frac{m_1 + m_2}{m_1 m_2} k_{12} + \frac{m_2 + m_3}{m_2 m_3} k_{23}\right)\lambda + \frac{k}{}$$

Its solution gives two values of λ and there
equation may be written as

$$\lambda^2 - b\lambda + c$$

and the roots are

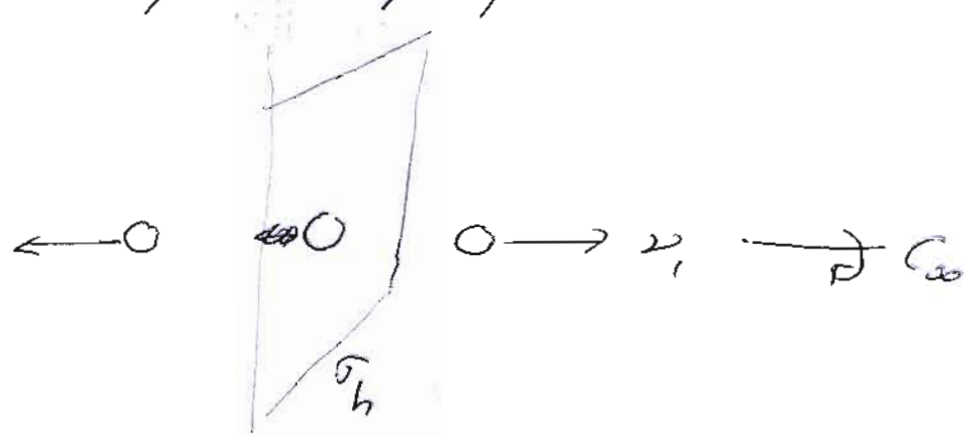
$$\lambda_1 = \frac{b - \sqrt{b}}{2}$$

and

normal modes transform with respect to the symmetry classes in the point groups of the molecules

~~charet~~ character table shows if a class is symmetric (+1) or antisymmetric (-1) to a symmetry operation

$D_{\infty h}$: CO_2



σ_h : vibration unchanged : +1

E : changes nothing anyway +1

C_∞ : changes nothing : +1

σ_v : " "

→ class Σ_g^+ or σ_g^+

E	σ_h	σ_v	i
1	1	1	1

inversion also changes nothing

no change in dipole moment → IR inactive

ν_2: $O \rightarrow$ $\leftarrow O$ $O \rightarrow$

σ_h reflects $\leftarrow O$ | $O \rightarrow$

on $\leftarrow O \rightarrow$ $\leftarrow O \rightarrow$

$\rightarrow$ σ_h -1

same for i: -1

σ_v, E: $+1$

E	σ_h	σ_v	i
$+1$	-1	$+1$	-1

$\rightarrow \Sigma_u^+ = \sigma_u^+$

$\rightarrow$ oscillating dipole moment $\rightarrow$ IR active

ν_3 ν_4 degenerate $\Rightarrow \pm 2$

σ_h: $+2$, E $+2$

σ_v: 0 because for ν_3, ν_4 it depends which one of the ∞ σ_v-planes

i: antisymmetric $\Rightarrow -2$

Π_u

oscillating dipole moment

$\rightarrow$ IR active

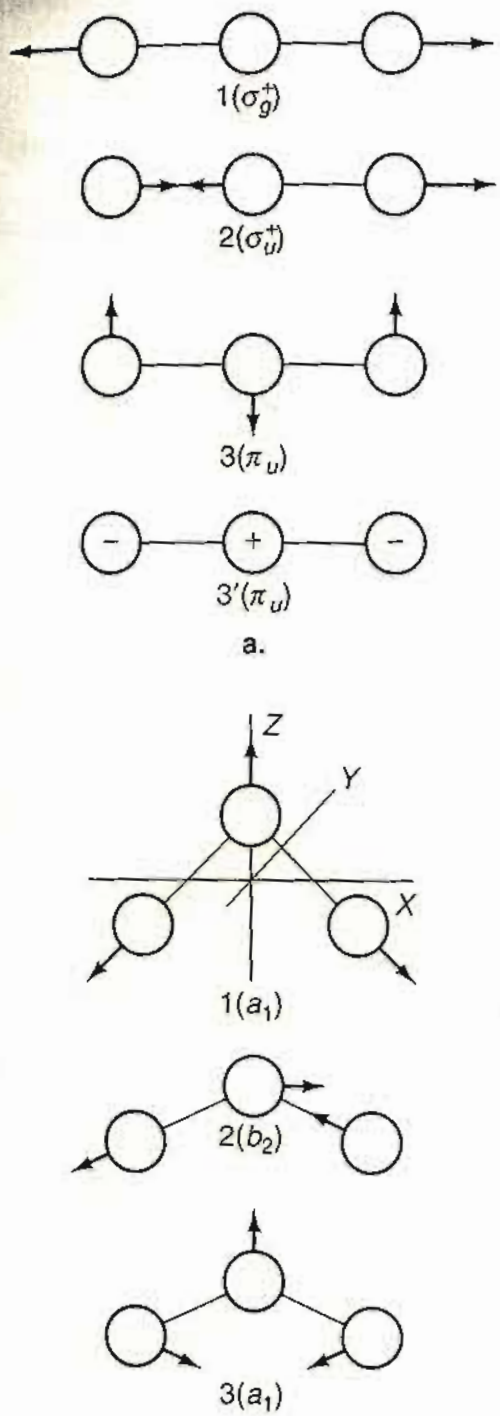


FIGURE 13.19
Normal modes of vibration. (a) The carbon dioxide molecule, which belongs to the point group $D_{\infty h}$. (b) The water molecule, which belongs to the point group C_{2v}. The character tables for these point groups are to be found in the appendix to Chapter 12 (pp. 577–579).

generally a large number of sets of bands c
transitions, because of the various vibrational
ferent normal modes of vibration. Each one of
corresponding to whether the rotational quan
level is lower or higher, respectively, than in th
is also allowed, and then there is additionally

The presence of infrared bands is restric
that a *diatomic* molecule can give a vibration
permanent dipole moment. This rule is a speci
for vibrational-rotational transitions, namely
give rise to an *oscillating dipole moment*. For
molecule to have a permanent dipole moment,
dipole moment, the moment remains zero th
possible for a more complex molecule initially
an oscillating moment during the course of its
normal modes of vibration of the carbon diox
In the purely symmetric mode the dipole mon
the vibration, and this vibration is not active
vibrations give rise to a small moment, and
spectrum, although it may be of weak intensi
other hand, produces an oscillating dipole m
from this motion. The carbon dioxide spectrun
is allowed, so that there is a Q-branch.

These symmetry restrictions may be form
seen that the normal modes of vibration m
species of the point group to which the m
molecule is vibrating in a normal mode and
moment μ. This dipole moment, being a vec
Z axes, and we can write these components
these components, μ_x, is affected by all th
as the normal mode of vibration itself. If thi
magnitude as the vibration occurs (i.e., will
hand, the component μ_x is of a different s
its magnitude will remain unchanged as the
components μ_x, μ_y, and μ_z are of different
be no oscillation of the dipole moment and
corresponding to that normal mode of vibra
components is of the same species as the
allowed, that is, the vibration is infrared ac

Since the components μ_x, μ_y, and μ
symmetry properties are the same as thos
The symmetry restriction can therefore be

There will be a vibrational-rotational
of vibration only if that mode belong

$D_{\infty h}$	E	σ_h	σ_v	i				
Σ_g^+	+1	+1	+1	+1			x^2+y^2	z^2
Σ_u^+	+1	−1	+1	−1	z			
Σ_g^-	+1	+1	−1	+1		R_z		
Σ_u^-	+1	−1	−1	−1				
Π_g	+2	−2	0	+2		$R_x\ R_y$	xz	yz
Π_u	+2	+2	0	−2	$x\ y$			
Δ_g	+2	+2	0	+2			x^2+y^2	xy
Δ_u	+2	−2	0	−2				
Φ_g	+2	−2	0	+2				
Φ_u	+2	+2	0	−2				

D_{6h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	σ_v			
A_1'	+1	+1	+1	+1	+1	+1			z^2
A_1''	+1	+1	+1	−1	−1	−1			
A_2'	+1	+1	−1	+1	+1	−1		R_z	
A_2''	+1	+1	−1	−1	−1	+1	z		
E'	+2	−1	0	+2	−1	0	$x\ y$		xy
E''	+2	−1	0	−2	+1	0		$R_x\ R_y$	$xz\ yz$

C_{2h}	E	C_2	σ_h	i				

KEY EQUATIONS

Heitler-London wave functions for

$$\psi_S = \frac{1}{\sqrt{2}}[1s_A(1)1s_B(2) + 1s_A$$

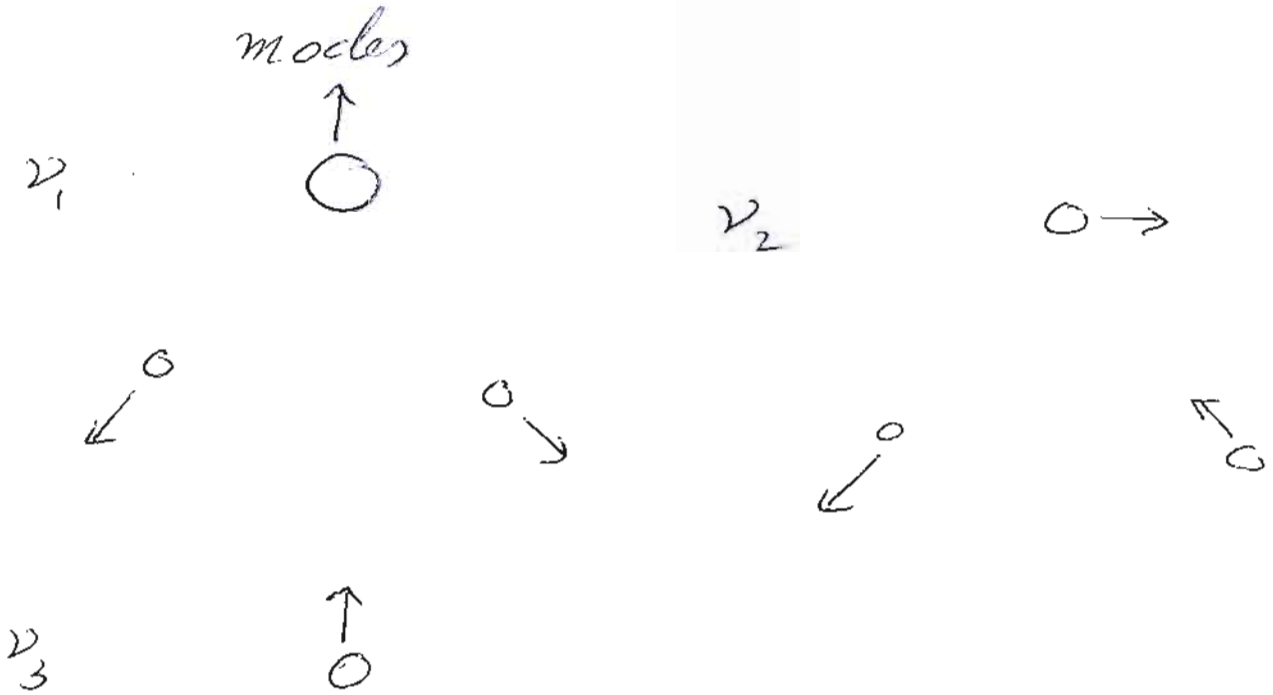
$$\psi_A = \frac{1}{\sqrt{2}}[1s_A(1)1s_B(2) - 1s_A$$

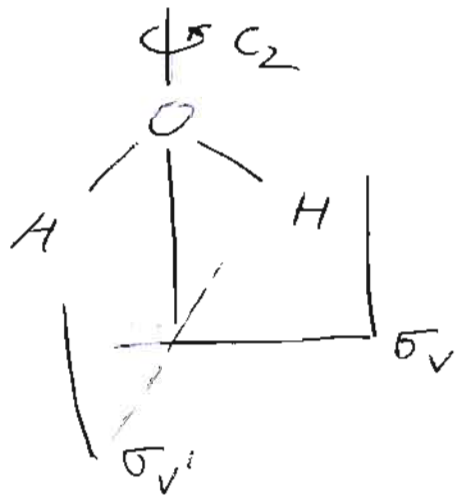
PROBLEMS

to give an IR-line,
a vibration must produce an
<u>oscillating</u> dipole moment in the
molecule
not a permanent one like necessary
for rotational spectra
so CO_2 has no permanent dipole,
but ν_2, ν_3, ν_4 produce an oscillating
one and thus IR lines
a diatomic molecule must have a
permanent dipole moment for a
vibration to be able to produce
an oscillating one.
If a vibration belongs to a symmetry
class to which also x, y or z in the
character table belongs is IR active

<u>H_2O</u> : permanent dipole moment
not linear

$\rightarrow 3N-6 = 3\cdot 3-6 = 3$ normal modes





ν_1 : no changes by E, σ_v and σ_v'

$\rightarrow +1, +1, +1, +1 \Rightarrow A_1$ or a_1

A_1 contains $z \Rightarrow \nu_1$ IR active

mechanisms of chemical reactions.

A difficulty that remains with the accurate quantum mechanical calculations is that even with supercomputers they still take a considerable amount of time if the molecule is of any complexity. It is necessary to use a large number of terms, perhaps a million, in the trial eigenfunctions to which the variational treatment is applied. Even though the final results may be of great importance, the methods employed do not shed any new light on the nature of the covalent bond. Our insights into the nature of the bond still have to come from the approximate treatments, mainly developed in the 1930s, that have been discussed in this chapter.

APPENDIX: CHARACTER TABLES

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$*					
A_1	+1	+1	+1	+1	z		x^2	y^2	z^2
A_2	+1	+1	−1	−1		R_z		xy	
B_1	+1	−1	+1	−1	x	R_y		xz	
B_2	+1	−1	−1	+1	y	R_x		yz	

*The modern convention is to take the $\sigma'_v(yz)$ plane to be the plane of the molecule.

C_{3v}	E	$2C_3$	$3\sigma_v$						
A_1	+1	+1	+1	z		x^2+y^2	z^2		
A_2	+1	+1	−1		R_z				
E	+2	−1	0	$x\ y$	$R_x\ R_y$	x^2-y^2	xy	xz	yz

$C_{\infty v}$	E	$\infty\sigma_v$				
Σ^+	+1	+1	z		x^2+y^2	z^2
Σ^-	+1	−1		R_z		
Π	+2	0	$x\ y$	$R_x\ R_y$	xz	yz
Δ	+2	0			x^2-y^2	xz

ν_2 : $E: +1$, $C_2 = z : -1$

$\sigma_v : +1$ (all moves in σ_v)

$\sigma_v' : -1 \rightarrow B_1$ or b_1

B_1 contains $x \Rightarrow$ IR active

ν_3 : $E: +1$ $C_2 : +1$

$\sigma_v : +1$ $\sigma_1' : +1$

$\rightarrow A_1$ or a_1

A_1 contains $z \Rightarrow$ IR active

<u>complicated molecules</u>

many vib. lines

each one with R, P branches ($\Delta J = \pm 1$)

<u>sometimes</u> (e.g. CO_2) Q-branch ($\Delta J = 0$) allowed

(Q mostly forbidden)

<u>diatomics</u> only those with permanent dipole can have an oscillating one upon vibration

only those with perm. dipole $\rightarrow$ spectrum

<u>CO_2</u> <u>no</u> permanent dipole moment

ν_1: upon oscillation μ always 0

→ no band

ν_2, ν_3, ν_4 create an oscillating μ

in ~~vib~~ vibration → band

CO_2: also Q branches ($\Delta J = 0$)

μ_x, μ_y, μ_z dipoles transform under

symmetry operations like x, y, z

⇒ if the symmetry class of a

vibration behaves like x, y, or z,

then it is active → band

mode; x, y, or z in same class → band

mode in class without x, y or z → no band

<u>CO_2</u>: $D_{\infty h}$: ν_1: Σ_g^+, no coord. → no band

ν_2: Σ_u^+, z coord. → band

ν_3, ν_4: Π_u, x, y coord. → band

H_2O C_{2v}

ν_1, ν_3 in A_1 and z → bands

ν_2 in B_2 and y → band

all modes → bands

see Figure: BF_3 D_{3h} H_2CO C_{2v}

ν_1 (a_1') inactive, no coordinate, BF_3

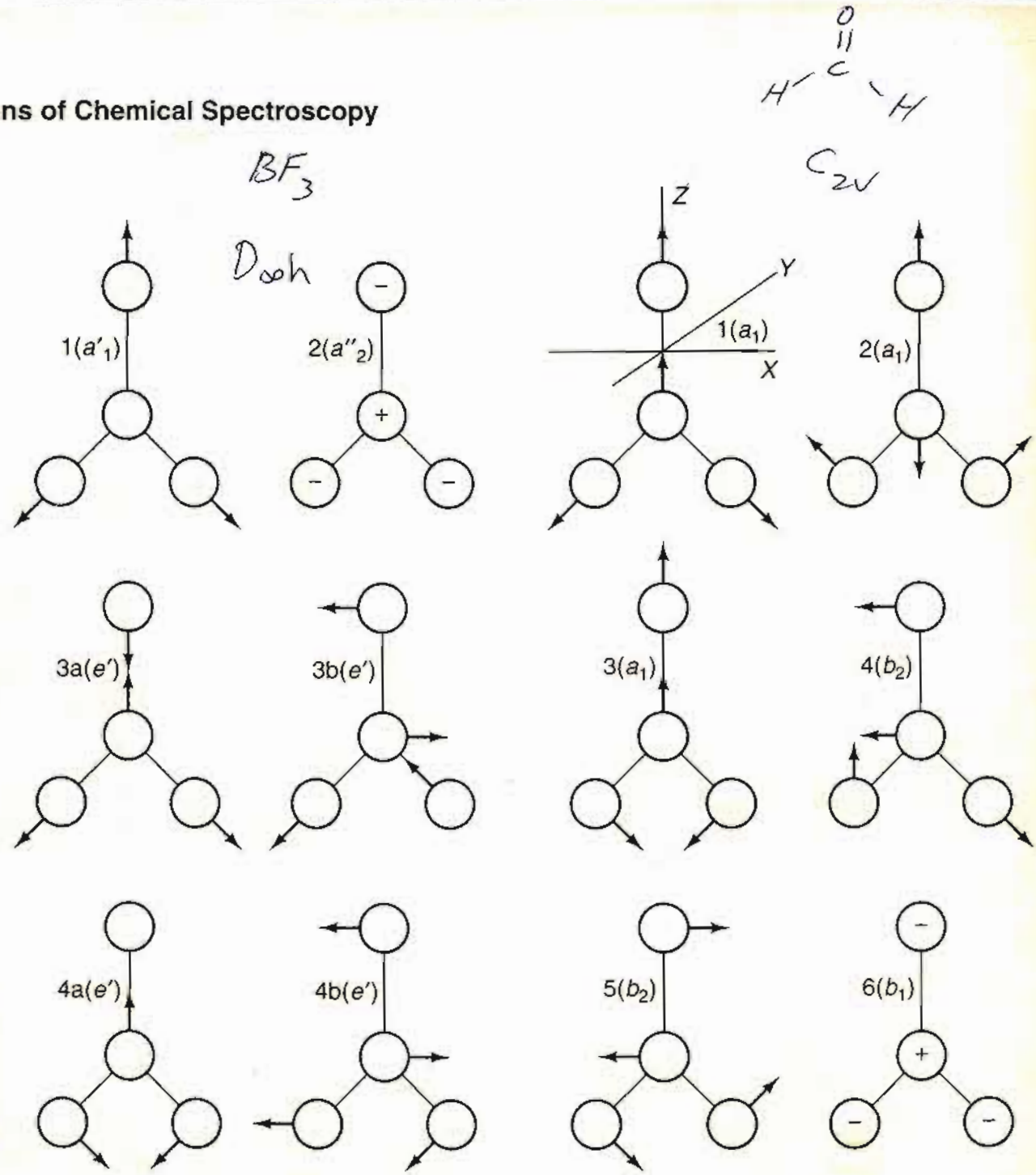
a_2'' (BF3), a_1, a_1 (H2CO) : z → active

e', e' : x, y → active BF_3

a_1 z active
b_2 y active } H_2O formaldehyde

$e'e'$ x, y active BF_3

b_2 y active
b_1 x active } H_2CO formaldehyd



of vibration
l molecule
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molecule
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79).

We may illustrate this rule by some examples. Consider first the normal modes of vibration for carbon dioxide, shown in Figure 13.19a. On p. 578 is an abbreviated character table for $D_{\infty h}$, which shows how the x, y, and z coordinates transform. The purely symmetric vibration is of symmetry species Σ_g^+ and is designated σ_g^+ (the lowercase letters are used); however, none of the coordinates belongs to this species,

Charcteristic group frequencies

bands of ~~some~~ many chemical groups appear in different molecules (also in complex ones) at similar wavenumbers and can indicate the presence of a specific group in an unknown molecule

TABLE 13.3 Characteristic Group Frequencies

Bond	Wavenumber, $\tilde{\nu}$ cm^{-1}	Wavelength, λ μm
O—H, N—H	3100–3500	3.2–2.85
C—H	2800–3100	3.6–3.25
C—O, C—N	800–1300	12.5–7.7
C=C, C=O	1600–1800	6.25–5.55
P—O	1200–1300	8.3–7.7

BF_3 (point group D_{3h}). The reader should verify the assignment of symmetry species for the vibrations and for the axes. Vibration 2 is of species a_2'', which is the same as z; it therefore gives rise to infrared bands. Vibrations $3a$, $3b$, $4a$, and $4b$ are e', as are x and y, so that these vibrations also give a spectrum. Vibration 1, however, is a_1', which does not correspond to x, y, or z; it therefore gives no spectrum.

Figure 13.20b is for a molecule like CH_2O, which belongs to the point group C_{2v}. The reader should verify that from the character table it can be deduced that all the normal modes give rise to an infrared spectrum.

Some of the selection rules for infrared and Raman spectra (Section 13.5) are conveniently summarized in the appendix to this chapter (p. 646). It should be noted that intuitive arguments, such as we used earlier for the vibrations of CO_2 (Figure 13.19a), are not reliable for more complicated systems.

Characteristic Group Frequencies

The complete analysis of the infrared spectrum of a molecule containing more than a dozen atoms is very difficult, and it is sometimes impossible. However, very useful information can be obtained from the spectra of quite large molecules if one makes use

$\leftarrow H-C\equiv N \rightarrow$

light H bound to heavy $C\equiv N$

$\Rightarrow \tilde{\nu}_1 = 2089\ cm^{-1}$

is mainly C-H stretch and not much affected by the rest

because H must move further than N to conserve the center of mass

multiple bonds: k larger than for single bonds $\rightarrow \tilde{\nu}$ larger

$\tilde{\nu}_2$ $3312\ cm^{-1}$ $H\rightarrow \leftarrow C\equiv N \rightarrow$

mostly $C\equiv N$ vibration

no 2 molecules have the same spectrum

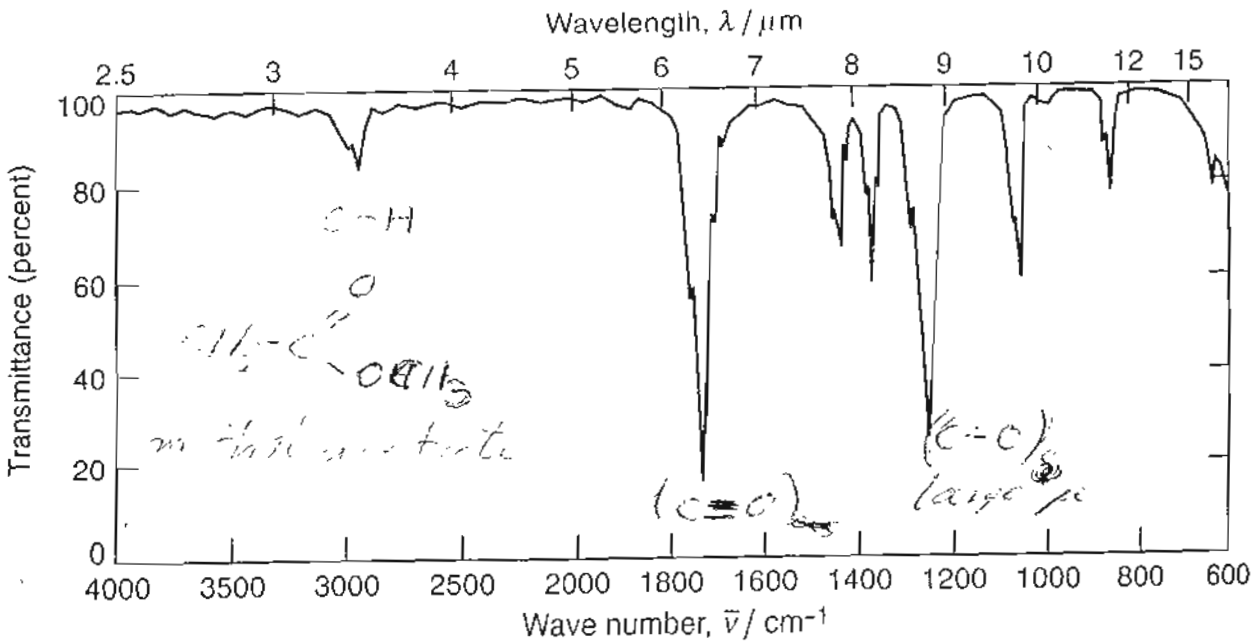
but functional groups can often be identified

$\rightarrow$ IR is a fingerprint spectrum

Bonds involving hydrogen atoms and multiple bonds therefore tend to have characteristic group frequencies. There are also some effects that work against characteristic group frequencies; the most important is when there is considerable symmetry so that the molecule contains two or more equivalent bonds. A simple example is provided by the water molecule (Figure 13.18b), which has normal mode frequencies of 3756, 3652, and 1595 cm^{-1}. The lowest of these may be attributed to the bending vibration. However, neither of the two higher frequencies can be ascribed to the stretching of one bond, since the two O—H bonds are equivalent. The stretching motions of the two bonds will therefore be strongly coupled, and in these two normal modes the two bonds stretch either in phase or out of phase with one another.

These limitations, however, are more prominent with fairly small molecules. With molecules of any complexity the characteristic group frequencies can provide useful supporting evidence for the presence of specific functional groups. Moreover, because

3.21
ed spectrum of methyl
his spectrum was ob-
the material in the liquid



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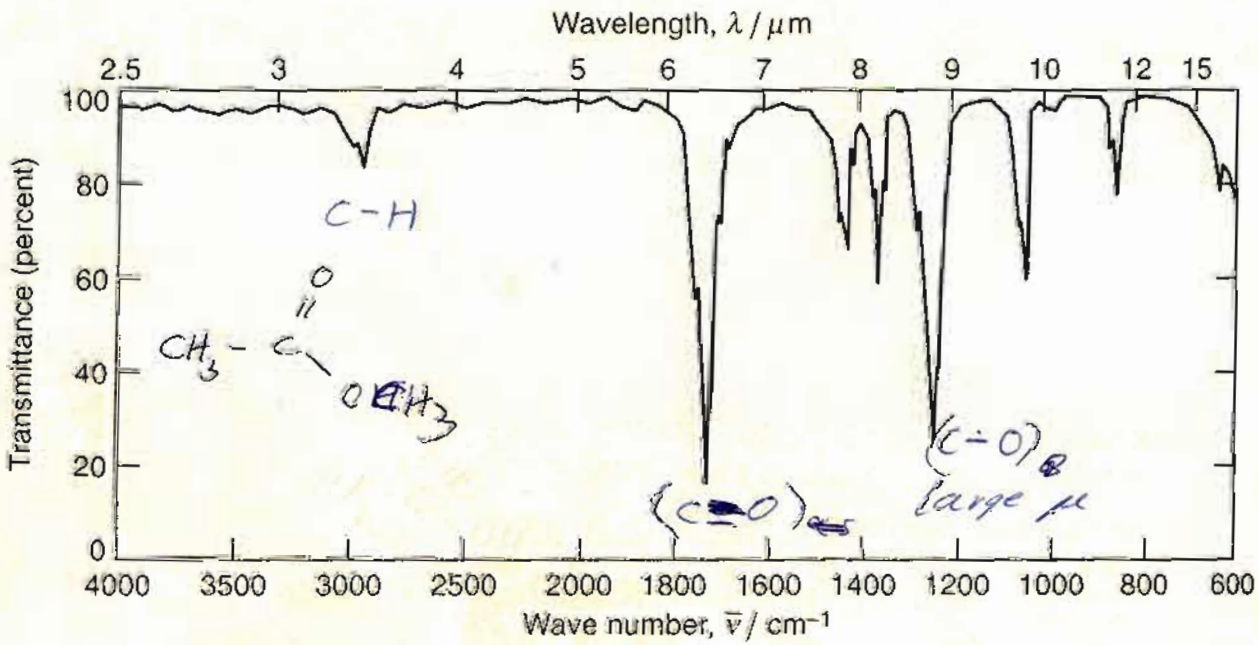
These limitations, however, are more prominent with fairly small molecules. With molecules of any complexity the characteristic group frequencies can provide useful supporting evidence for the presence of specific functional groups. Moreover, because

methylacetate ~~Meth-O-Meth~~

13.21
red spectrum of methyl
This spectrum was ob-
h the material in the liquid



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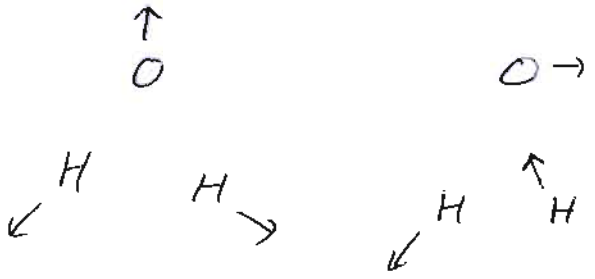
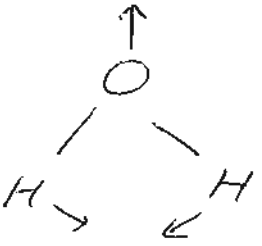
<u>but</u> H_2O: both O-H equivalent

→ no individual O-H stretch

only symmetric and antisymmetric stretches at 3756 and 3652 cm^{-1}



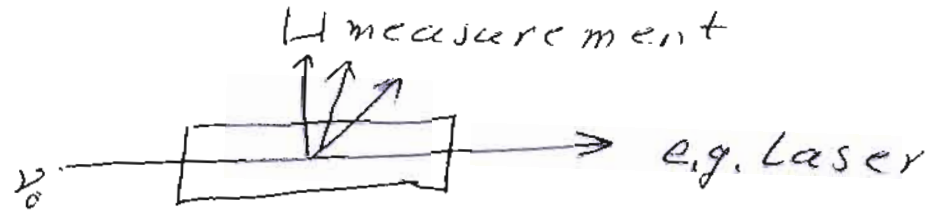
bend at 1595 cm^{-1}



Obj Raman spetra
Electronic spectroscopy

Raman spectra

Light is scattered in a medium (sample)



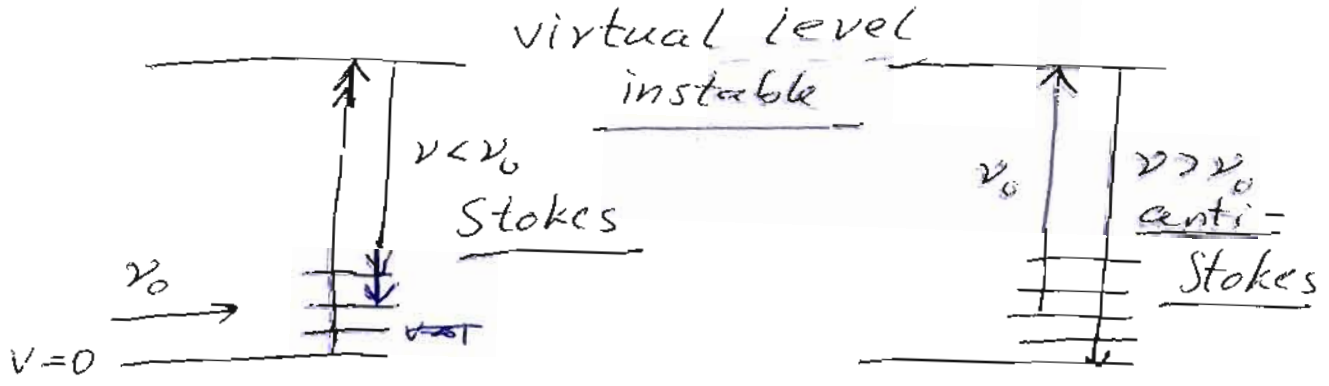
most of the scattered light has ν_0 unchanged: Rayleigh scattering

Intensity $\sim \nu_0^4$

But a part of the light has $\nu > \nu_0$ (anti-Stokes)

and another part $\nu < \nu_0$ (Stokes)

ν_0 must be monochromatic light



shift:
energy difference of rotational and vibrational levels

2-photon process (other selection rules than 1-photon ones, IR absorption)

$$\Delta J = 0, \pm 2$$

$$\Delta V = \pm 1, \pm 2, \ldots \text{ anharmonic oscillator}$$

strongest vibrational Raman band:

$$V=1 \leftarrow V=0$$

almost only one populated

<u>stokes</u>: $\nu = \nu_0 - \frac{|\Delta E|}{h}$ $\quad \nu < \nu_0$

$\Delta E < 0$

<u>anti-stokes</u>: $\nu = \nu_0 + \frac{|\Delta E|}{h}$ $\quad \nu > \nu_0$

$\Delta E > 0$

ΔE here: initial − final

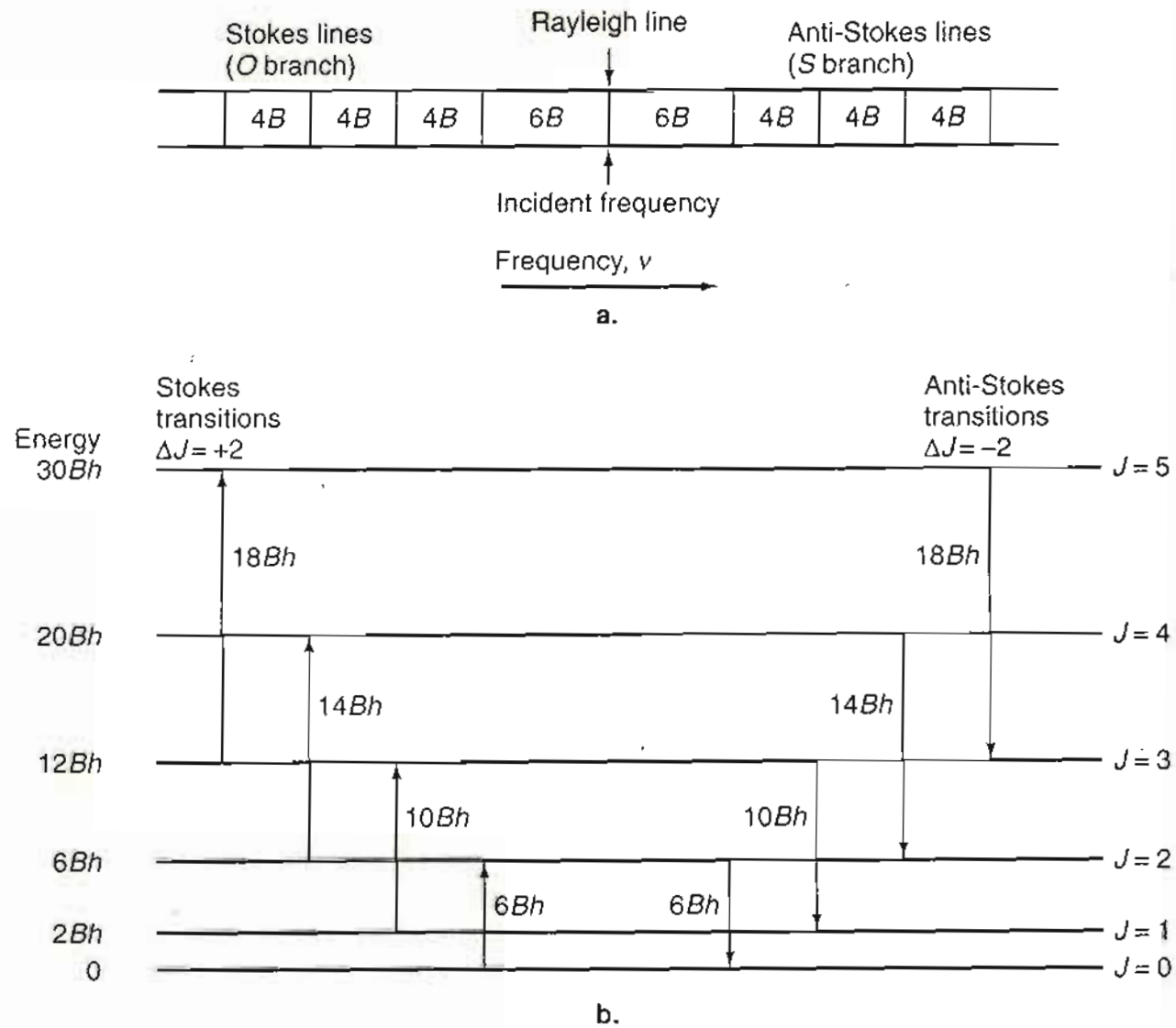
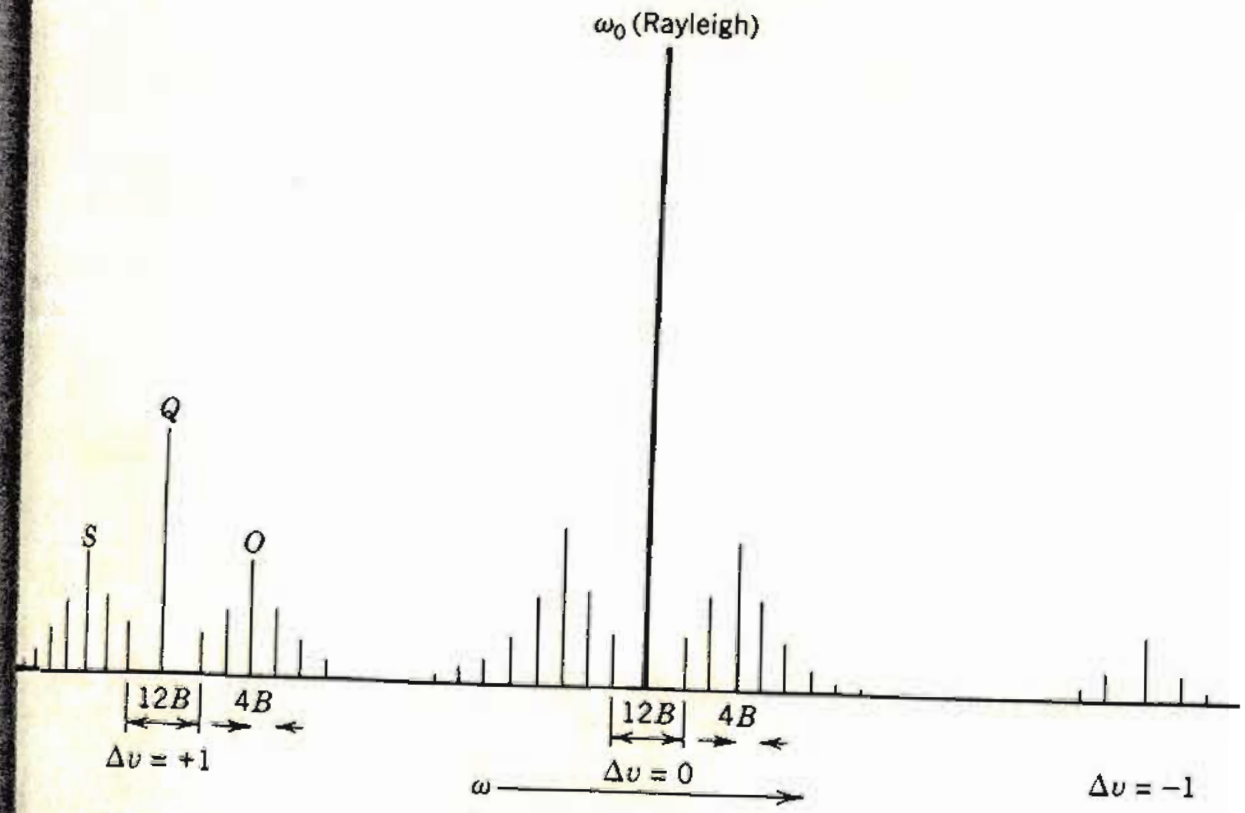


FIGURE 13.22
(a) Schematic representation of a Raman spectrum arising from pure rotational transitions. (b) The rotational transitions giving rise to Raman lines.

of these lines is

$$\nu = \nu_0 + \frac{\Delta E}{\ldots} \tag{13.125}$$



gure 14.14 Theoretical rotation–vibration Raman spectrum of a linear molecule. e effects of nuclear spin statistics have been omitted from this illustration. (W. A. allory, *Introduction to Molecular Structure and Spectroscopy*. Boston: Allyn & con, 1977, by permission.)

gure 14.14 shows the theoretical rotation–vibration Raman spectrum for Δv +1, 0, −1 and ΔJ = +2, 0, −1 for a linear molecule. It is assumed that re is a small population in the first excited vibrational state. The center ies of lines is the rotational Raman spectrum of the molecule. Since hom-

than the initial state, many Raman spectral lines can be observed. A typical experimental apparatus is shown in Fig. 14.10 and a Raman spectrum of liquid CCl_4 is shown in Fig. 14.11. The spectral lines with $\nu' < \nu$ are called **Stokes lines** and those with $\nu' > \nu$ are called **anti-Stokes lines.** The Stokes lines are produced when the light loses energy to the molecule and the anti-Stokes lines are produced when the light gains energy from the molecule. Therefore, anti-Stokes lines are caused when the molecule in a higher energy state makes a transition to a lower state. Since the population of molecules in high-energy

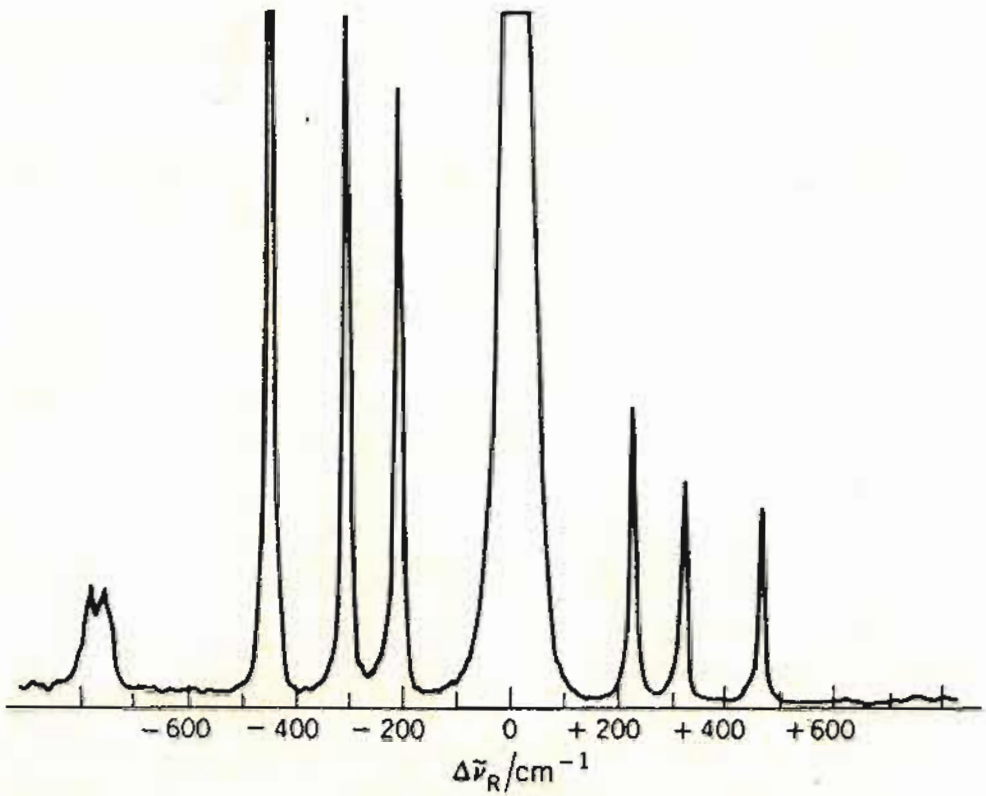


Figure 14.11 Raman spectrum of liquid CCl_4 obtained using a He–Ne laser. The Raman frequencies are measured from the parent line at 632.8 nm. In this spectrum frequency increases to the right so that the lines to the left of the laser line have a lower frequency; they are called Stokes lines.

anti-Stokes line are weaker than the Stokes lines

→ usually Stokes used in spectroscopy

ν_0 : Rayleigh line

in spectra usually shift $\Delta\nu$ from Rayleigh line given

in rot./vib. spectra:

P, Q, R branches all present

<u>rotational rule</u>: $\Delta J = \pm 2$ (pure rot.)

<u>$\Delta J = +2$</u> $|\Delta E| = |E_{J+2} - E_J| = hB(4J+6)$

$$\rightarrow \tilde{\nu} = \tilde{\nu}_0 - \tilde{B}(4J+6) \quad J \geq 0$$

S-branch (Stokes part $\nu < \nu_0$)

<u>$\Delta J = -2$</u> $|\Delta E| = |E_{J-2} - E_J| = hB(4J-2)$

$$\tilde{\nu} = \tilde{\nu}_0 + \tilde{B}(4J-2) \quad J \geq 2$$

O-branch (anti-Stokes part)

both $6\tilde{B}$ away from $\tilde{\nu}_0$: first lines

S: $J=0$ O: $J=2$

$\tilde{\nu}_0 - 6\tilde{B}$ $\tilde{\nu}_0 + \tilde{B}(2 \cdot 4 - 2) = \tilde{\nu}_0 + 6\tilde{B}$

line spacing: $4\tilde{B}$

in CCl_4 the Stokes lines are at
$\Delta\tilde{\nu}_1$, $\Delta\tilde{\nu}_2$ $\tilde{B}$?

$\tilde{B} = \frac{1}{6}|\Delta\tilde{\nu}_1|$ or $\tilde{B} = \frac{1}{4}|\Delta\tilde{\nu}_2 - \Delta\tilde{\nu}_1|$

Intensities of these lines:
Stokes (S branch) I_1^S, I_2^S

ant-Stokes (O branch) I_1^O, I_2^O

Intensity ratios $\rightarrow T$
I_1^S $(0 \rightarrow 2) \sim N_0$ (population of level 0)
I_1^O $(2 \rightarrow 0) \sim N_2$ (population of level $J=2$)
ratios:

$$\frac{N_2}{N_0} = \frac{I_1^O}{I_1^S} = (2J+1)\, e^{-\frac{hc\tilde{B}}{k_B T} J(J+1)}$$

$\underline{J=2}$

$2J+1 = 5$ $(J=2)$, $J(J+1) = 6$

$$\rightarrow \frac{hc\tilde{B}}{k_B T} \cdot 6 = \ln \frac{I_1^S \cdot 5}{I_1^O}$$ reverse ration because - sign

$$T = \frac{hc\tilde{B}\cdot 6}{k_B}\left[\ln \frac{5 I_1^S}{I_1^O}\right]^{-1} \quad J=2$$

2 advantages

1) no IR or microwave needed

line frequencies are shifts from incident ν_0 which can be even visible light

also solutions in water can be used i ν_0 where water does not absorb

it would absorb all IR light

2) lines forbidden in IR are allowed in Raman and the reverse

different rule:

for Raman spectra

not ~~the~~ a dipole moment must oscillate with vibration

but the polarizability must oscillate

$\underline{H_2O_2}$: no IR

no microwave spectra

but Raman spectra

polarizability measures how easy an electron cloud can be distorted

H_2, O_2: compress a bond in a vibration and it is more hard to move the electrons in it (stronger) while a elongated bond is weaker

induced dipole moment:

$$\vec{\mu}_{ind} = \underline{\underline{\alpha}}\,\vec{E}$$

light: $\vec{E} = \vec{E}_0 \sin(2\pi\nu_0 t)$ (incident)

$$\rightarrow \vec{\mu}_{ind} = \underline{\underline{\alpha}}\,\vec{E}_0 \sin(2\pi\nu_0 t)$$

$\underline{\underline{\alpha}}$: polarizability tensor (matrix)

change by vibration:

$$\underline{\underline{\alpha}} = \underline{\underline{\alpha}}_0 + \underline{\underline{R}} \sin(2\pi\nu_{vib} t)$$

$\vec{\mu}$ oscillates with $\nu_0 \pm \nu_{vib}$

and sends out light

(Stokes, anti-Stokes)

$$\underline{\underline{\alpha}} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \qquad \begin{aligned} \alpha_{yx} &= \alpha_{xy} \\ \alpha_{zx} &= \alpha_{xz} \\ \alpha_{zy} &= \alpha_{yz} \end{aligned}$$

→ <u>If</u> in the character table of the symmetry group of the molecule a vibration appears in a class that has also

$x^2, y^2, z^2, xy, xz,$ or yz in it,

then the vibration is Raman active → line

Σ_g^+, Π_g, A_g Raman active

$D_{\infty h}$	E	σ_h	σ_v	i			
Σ_g^+	+1	+1	+1	+1			x^2+y^2 z^2
Σ_u^+	+1	−1	+1	−1	z		
Σ_g^-	+1	+1	−1	+1		R_z	
Σ_u^-	+1	−1	−1	−1			
Π_g	+2	−2	0	+2		R_x R_y	xz yz
Π_u	+2	+2	0	−2	x y		
Δ_g	+2	+2	0	+2			x^2+y^2 xy
Δ_u	+2	−2	0	−2			
Φ_g	+2	−2	0	+2			
Φ_u	+2	+2	0	−2			

Σ_u^+, Π_u IR active

D_{6h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	σ_v			
A_1'	+1	+1	+1	+1	+1	+1			z^2
A_1''	+1	+1	+1	−1	−1	−1			
A_2'	+1	+1	−1	+1	+1	−1		R_z	
A_2''	+1	+1	−1	−1	−1	+1	z		
E'	+2	−1	0	+2	−1	0	x y		xy
E''	+2	−1	0	−2	+1	0		R_x R_y	xz yz

C_{2h}	E	C_2	σ_h	i	

KEY EQUATIO

Heitler-London wa

$$\psi_S = \frac{1}{\sqrt{2}}[1s_A$$

$$\psi_A = \frac{1}{\sqrt{2}}[1s_A$$

PROBLEMS

Electronic spectra

visible, ultra violet (UV) light

together with electronic transitions

rot./vib. transitions appear

gas phase: sharp, well defined bands (vib.) and fine structures (rot.)

in solution: broad absorptions corresponding to el./vib./rot. transitions

every substance has an electronic spectrum

no matter if dipole moment or polarizability changes

Terms for linear molecules

atoms: analogous labels

but for <u>linear</u> molecules

<u>here</u> axial angular momentum
important: $\Lambda\hbar$ ($\hat{=}$ $M\hbar$ in atoms)

<u>atoms</u>: total angular momentum
L important

e-cloud: $\Lambda = 0$ cylinder symmetry

$\Lambda = 0 \rightarrow \Sigma$ term

$L=0$	S	$\Lambda=0$	Σ
$L=1$	P	$\Lambda=1$	Π
$L=2$	D	$\Lambda=2$	Δ
$L=3$	F	$\Lambda=3$	ϕ
atoms		linear molecules	

LiH: $C_{\infty v}$

$\rightarrow \Sigma^+$ or Σ^-

if e-cloud is symmetric (+) or antisymmetric to a σ_v-plane (one of the ∞ # of σ_v planes)

O_2: $D_{\infty h}$

$\Sigma_g^+, \Sigma_u^-, \Sigma_g^-, \Sigma_u^+$

g: e^--cloud symmetric to inversion center i

u: e^- cloud antisymmetric to inversion center i

capital greek letter: Λ

upper left corner: spin multiplicity $2S+1$ of molecule

upper right corner: symmetry to a σ_v ~~axis~~ plane (+ for symmetric, − for antisymmetric

lower right corner: symmetry to the inversion center i (g for symmetric, u for antisymmetric)

<u>only</u> if the molecule has i

$\underline{H_2}$: $\uparrow\downarrow \rightarrow S=0, \quad 2S+1=1$
singlet

no angular momentum: $L_z=0$ (along z: only important component)

$\Lambda = 0$

σ_v e^--cloud (σ-MO) does not change sign $\rightarrow$ +
and is symmetric to i $\Rightarrow$ g

$\rightarrow {}^1\Sigma_g^+$

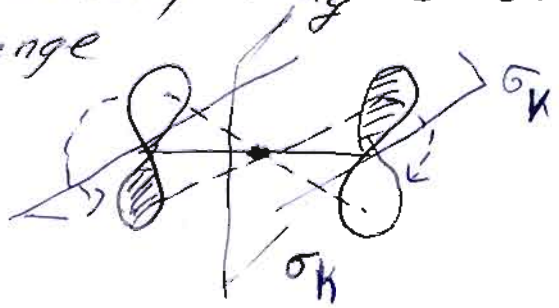
general: $^{2S+1}\Lambda^{\pm}_{g,u}$ ($\pm \leftarrow \sigma_v$, $g,u \leftarrow i$)

$\underline{O_2}$: 2 unpaired electrons
$\longrightarrow 2S+1 = 3$

π orbitals

for the unpaired electrons (highest ones count): π_g^* orbitals

sign change on σ_v $\rightarrow$ −



~~si~~ no sign change in i: g

π electrons are outside the molecular axis (perpendicular

$\rightarrow$ no angular momentum along z

$\rightarrow \Lambda = 0 \Rightarrow {}^3\Sigma_g^-$ ground state

write $X\,{}^3\Sigma_g^-$ because it is the groundstate for triplet states

~~$X\,{}^2\Pi_g$: groundstate for the doublet states~~

capital letters A, B, C

given to excited states of same 2S+1 tye as the ground state

lower case letters a, b, c

to excited states of different 2S+1 type

X A, B, C

increasing energy

a, b, c

Obj selection rules

structure of band systems

Birge - Spooner method

Selection rules

for light molecules (linear)

$\Delta\Lambda = 0, \pm 1$, $\Delta S = 0$ as atoms

in case of $\Sigma \leftrightarrow \Sigma$: $+ \leftrightarrow +$, $- \leftrightarrow -$ allowed

$+ \not\leftrightarrow -$ forbidden

Laporte rule for molecules with i:

$g \leftrightarrow u$ allowed

$g \not\leftrightarrow g$, $u \not\leftrightarrow u$ forbidden

many exceptions, specially in heavy molecules

O_2 $B\,^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ $\Delta\Lambda = 0$ (31)-2

$- \leftarrow -$, $u \leftarrow g$

very intense, allowed Schumann-Runge bands at ≈ 200 nm

$\Pi \leftarrow \Sigma$ $\Delta\Lambda = 1$ allowed

$\Delta \leftarrow \Sigma$ $\Delta\Lambda = 2$ forbidden

forbidden bands are also observed, but with very weak intensity:

vis.: 760 nm $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$

IR: 1300 nm $^1\Delta_g \leftarrow {}^3\Sigma_g^-$

vibrations that destroy the symmetry of states can make a forbidden el. transition allowed

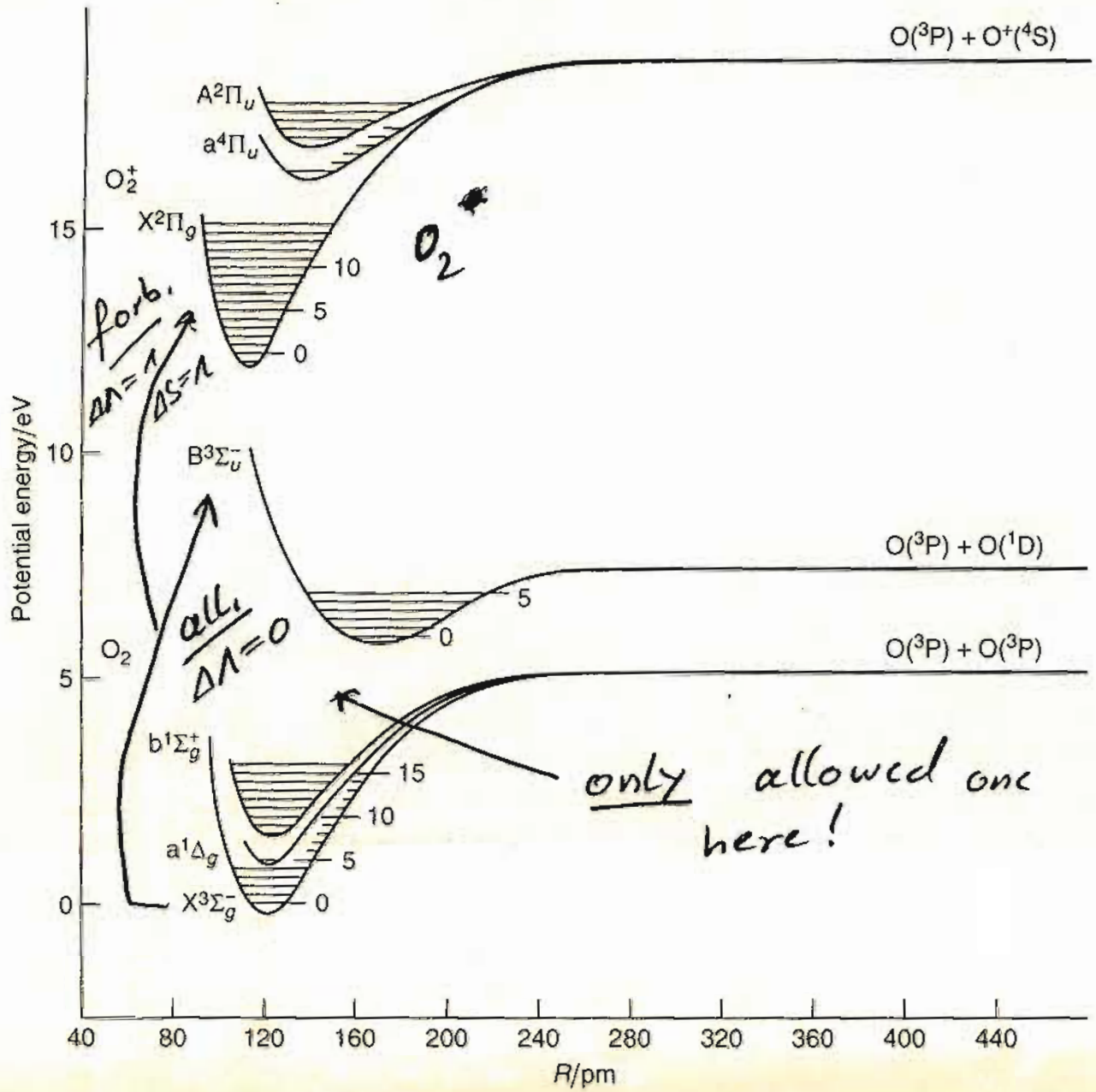


FIGURE 13.23
Potential energy diagram for O_2. Not all vibrational states are shown. (Gilmore, Forrest R., *Potential Energy Curves for N_2, N_0, O_2, and Corresponding Ions*, RAND, RM-4034-1-PR, April 1966. Used by permission.)

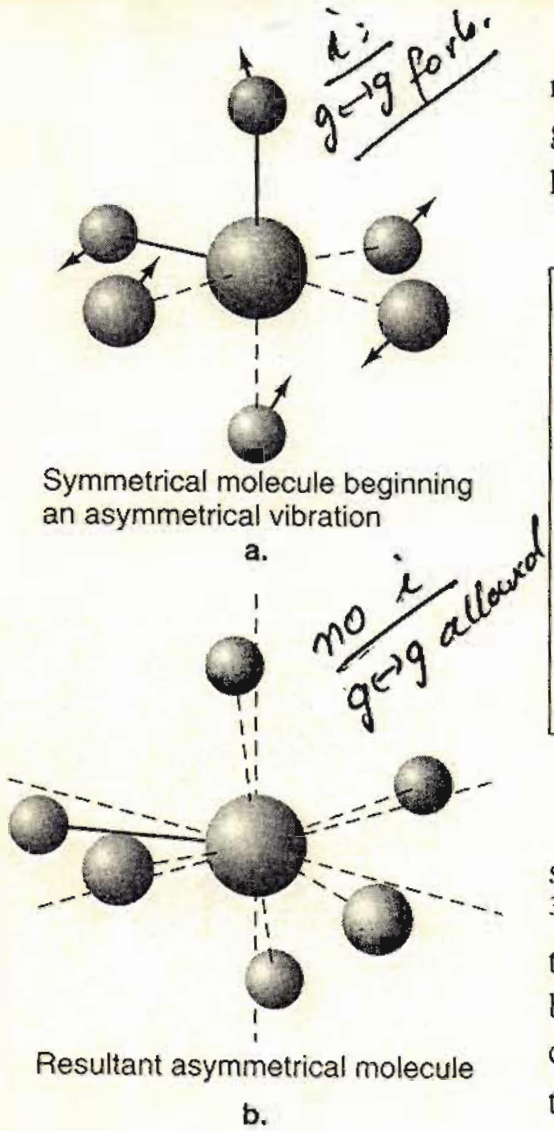


FIGURE 13.24
A centrosymmetric complex is parity forbidden in (a) from having a d ↔ d transition. An asymmetric vibration (b) removes the center of inversion and a $e_g \leftarrow t_{2g}$ transition becomes weakly allowed.

d–d is same parity
g↔g

metric complex destroys the center of symmetry allowi
g ↔ g transition. This distortion allows a d ↔ d transit
plex shown.

EXAMPLE 13.9 From Fig. 13.23, list the allowed ele
from the ground state to the excited states of O_2 that are pe
selection rules.

Solution According to the selection rules, starting with
from the Σ state to a Σ state is permitted as well as to
However, the excited $^2\Pi_g$ state is of an oxygen molecule i
Only a triplet state to a triple state transition is permitt
eliminate all transitions shown except the transition to the
is permitted as well as − ↔ −.

The strongest bands in the absorption spectrum of t
so-called *Schumann-Runge* bands, at about 200 nm, ai
$^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$. This is the transition that is allowed in th
the selection rules previously given. The oxygen spectrum
bands that violate the selection rules. For example, at abou
due to a $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition, and there are very weak
that arise from a $^1\Delta_g \leftarrow {}^3\Sigma_g^-$ transition. In both of these tra
of multiplicity, and both violate the g ↮ g prohibition.

It is of some interest to note that these two excited st
visible and in the infrared range. But in spite of the larg
the atmosphere, only a small fraction of the solar radiatio
removed. This shows that the selection rule that transitions c
of like multiplicity is very strongly obeyed.

The Structure of Electronic Band Systems

Since electronic spectra also involve vibrational changes,
bronic spectra. Each band in a vibronic spectrum is asso
vibrational energy and consists of many closely spaced rot
have on one side a sharp edge, or *band head*. Beyond this
falls sharply to zero, while on the other side of the band th
gradually and is said to be *shaded* or *degraded*.

In the Born-Oppenheimer approximation each electr
molecule is represented by a curve showing potential ene
nuclear distance. On this curve the various vibrational st
horizontal lines. For a molecule containing more than two a
principle be represented by a multidimensional surface in w
is plotted against a number of distances and angles that spe

structure of band systems

in el. transitions
also vib. transitions

→ vibronic band system

each band ~~had~~ has closely spaced rot. lines in it

on one ~~sy~~ side of the band:
sharp end of the bands
band head

other side: intensity decreases gradually to higher ν
shaded or degraded region

Born-Oppenheimer approx.

diatomics: ~~ech~~ each electronic state has a potential curve with vibrational levels as lines plotted in it

> 2 atoms:

E_p depends on many coordinates:
$3N-6$

can be a very complex
multi-dimensional surface
hypersurface

but the basic ideas are the same as for diatomics

room temp.:
almost all molecules are in their electronic groundstates and in $v''=0$

→ absorption shows a series of bands for 2 electronic states:

0-0 $v'=0 \leftarrow v''=0$

1-0 $v'=1 \leftarrow v''=0$

2-0 $v'=2 \leftarrow v''=0$

<u>emission</u> : first excitation (el./vib)

must happen

<u>then</u> many more bands when

falling back to the ground

state

<u>Franck-London principle</u>

el. transition : $10^{-15} - 10^{-18}$ s

vib. " : $\approx 10^{-13}$ s

→ in an electronic transition

the geometry is not changed

→ vertical transition between

2 potential curves

intensity ~ overlap of the

vibrational function ~~at~~

~~the transition geometry~~

largest I, when the center of

the initial state is in a region

of same sign in the final state

The transitions corresponding to these bands are shown in Figure 13.25. Such a series of bands is called a *progression*, a each band is usually labeled $v'-v''$ with the *upper* state given first; the absorption bands indicated here would thus be labeled, 0–0, 1–0, 2–0. For an emission spectra to be studied, however, energy must be supplied to the system in some way, with the production of electronically excited species in which higher vibrational levels may be populated. Transitions from these levels can occur to vibrational levels in the electronic ground state, and some of these

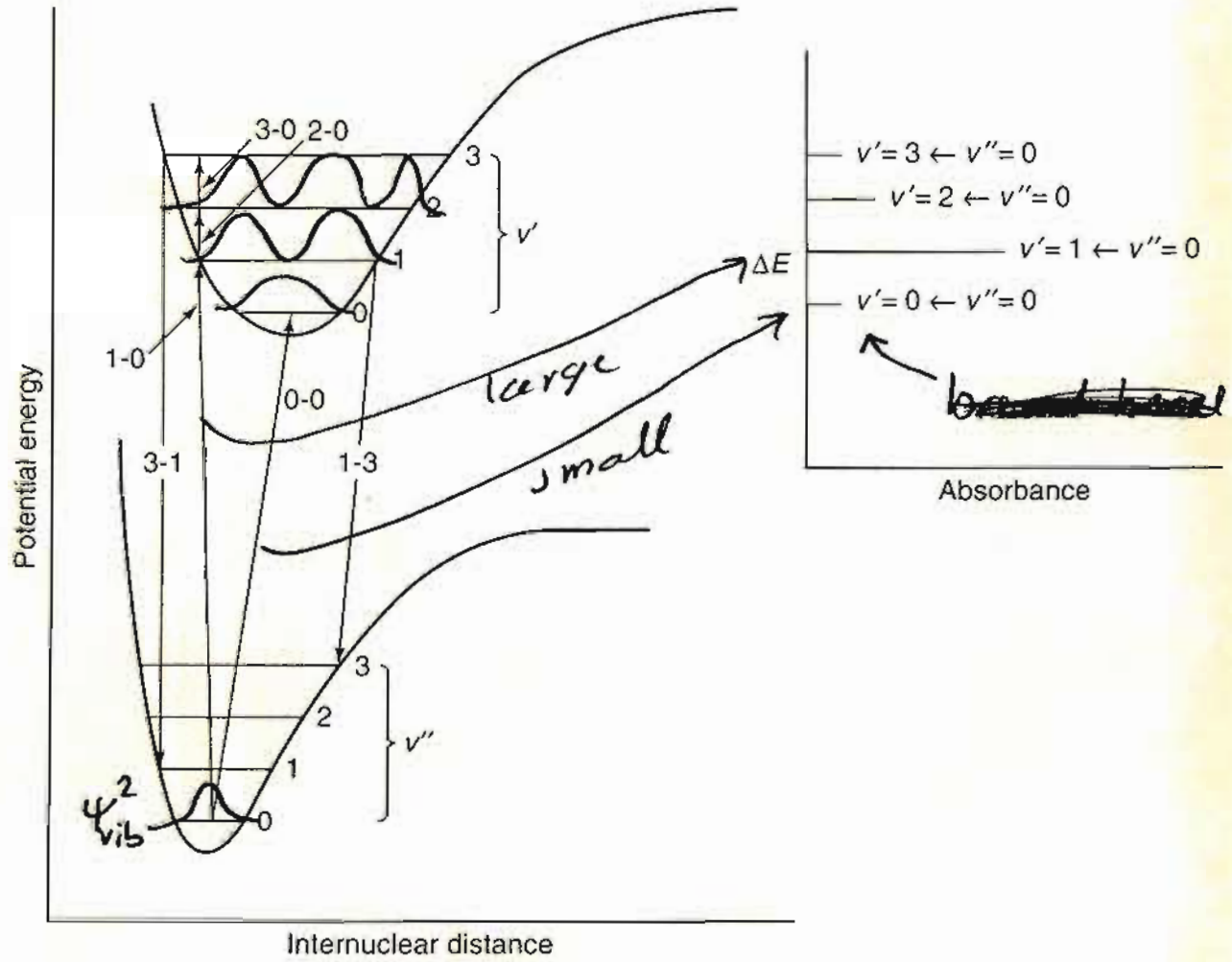
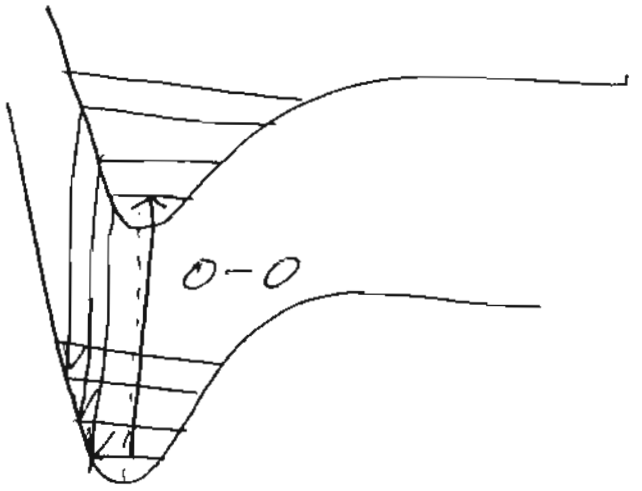


FIGURE 13.25
Two electronic states of a diatomic molecule, showing a number of vibrational levels. Transitions giving rise to absorption bands (↑) and to emission bands (↓) are shown.

if strong $0 \leftarrow 0$ absorption
& strong $0 \leftrightarrow 0$, $1 \rightarrow 1$, $2 \rightarrow 2$ emission

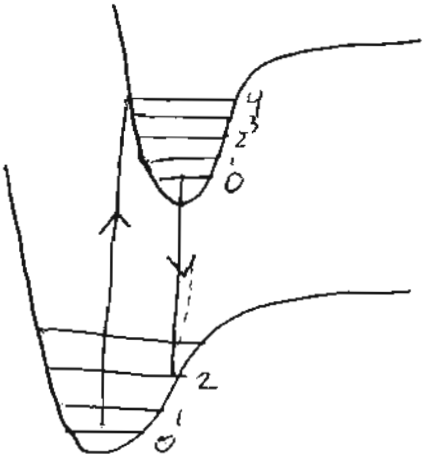
$\rightarrow$ similar curves

minima above each other



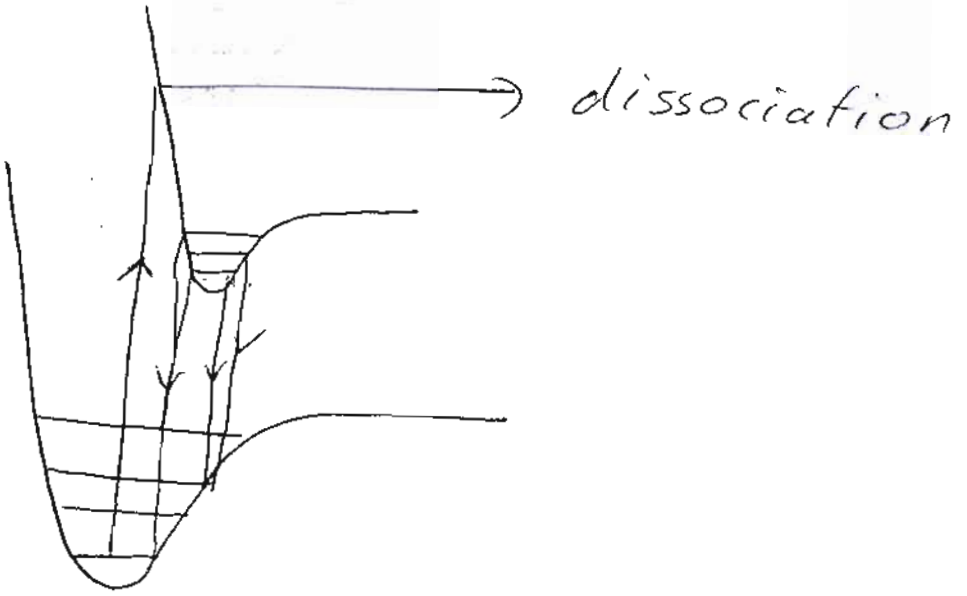
if strong $4 \leftarrow 0$ absorption
strong $0 \rightarrow 2$ ~~absorption~~ emission

upper ~~min~~ $v=0$ center must be at the edge of lower 2
lower $v=0$ must be at the edge of upper 4



no rotational fine structure in absorption:
sharp emissions

→ in absorption the molecule dissociates immediately



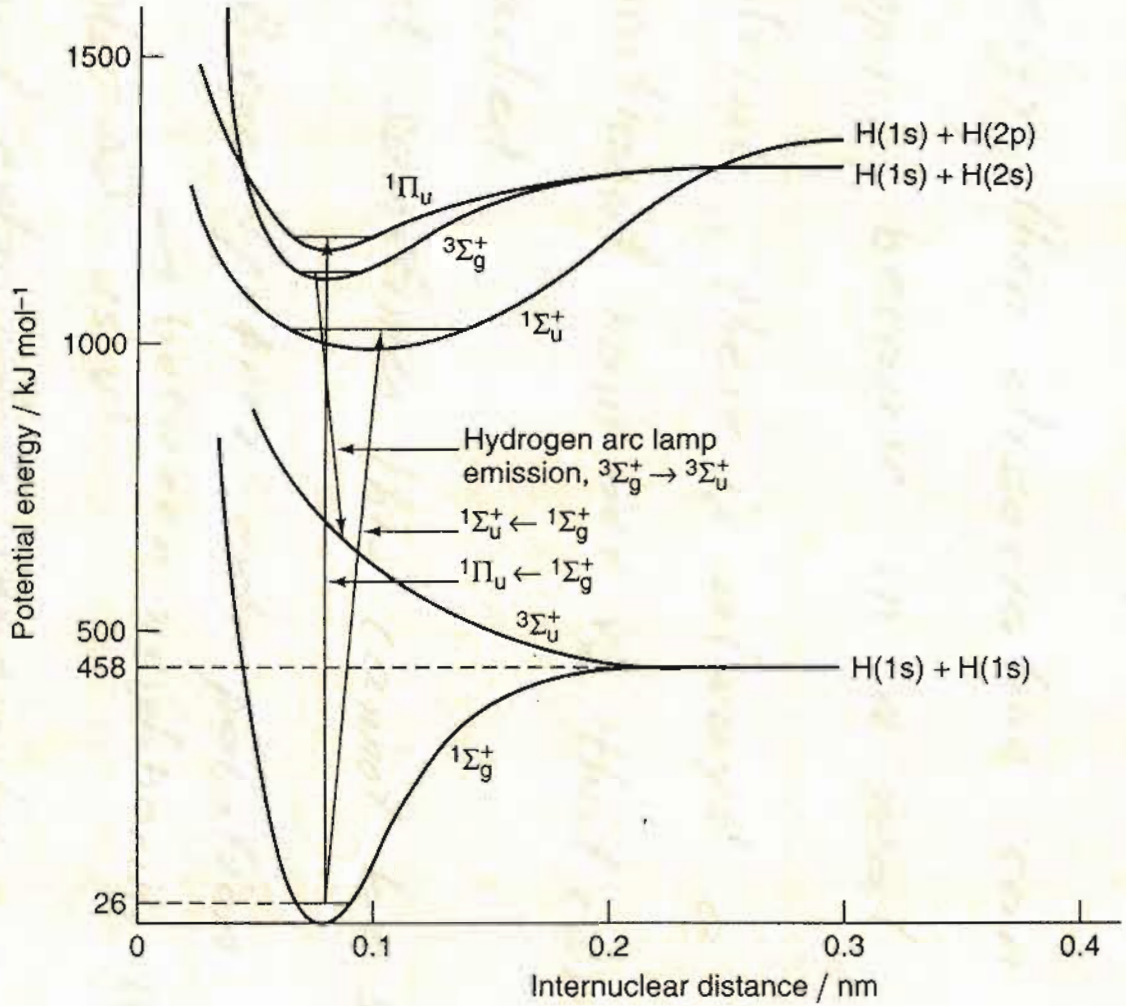


FIGURE 13.26
Schematic potential-energy curves for the ground state and some excited states of the hydrogen molecule. Lines representing absorption from v'' are displaced from vertical for clarity.

probabilities at other positions in $v'' = 0$, so the weaker transitions occur from those positions also. These transitions have the effect of changing the lines shown in the absorbance shown in Figure 13.25 into a broader spectrum.

Excited Electronic States

If transition to high in energy then dissociation can happen, because in a real molecule, there is always a largest vibrational number v'_m that can be reached

but sometimes this cannot be seen

→ Birge-Sponer extrapolation

plot $\Delta\tilde{\nu}$ vs v' → between neighboring lines

and extrapolate linearly.

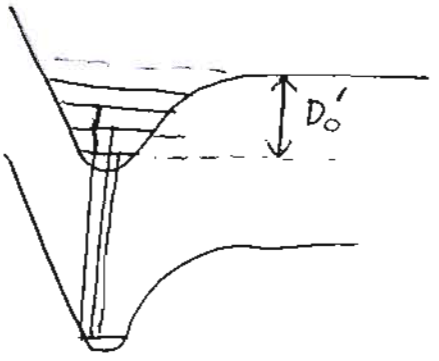
Then the intercept on the v' axis is v'_m because at diss. the lines are most dense and thus $\Delta\tilde{\nu} = 0$

The area under the curve is the dissociation energy

area under $\Delta\tilde{\nu}$

→ Σ of level splits

→ D_0'



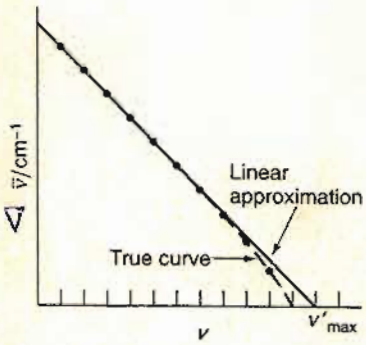


FIGURE 13.27
A Birge-Sponer extrapolation to find v'_{max} and the dissociation energy. Energies in cm^{-1} are plotted against their corresponding vibrational quantum numbers.

rather rigorously to a molecule as light as hydrogen. The absorption spectrum of H_2 shows bands corresponding to the $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ and $^1\Pi_g^+ \leftarrow {}^1\Sigma_g^+$ transitions. In a hydrogen arc lamp, molecules are produced in the $^3\Sigma_g^+$ state, and the characteristic emission is due to the transition $^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$. Information from these states can be used to determine dissociation energies as earlier discussed on page 620.

It is possible to find the dissociation energy when several lines arise in vibronic transitions. The idea is that the energies of each contributing vibrational level sum to give the dissociation energy. However, some of the vibrational levels out to the dissociation limit may not be visible. A useful approximation is to use the *Birge-Sponer extrapolation*. A plot of the energy in cm^{-1} is made against the vibrational quantum number, v. A straight line extrapolation of observed values is made to obtain the intercept on the abscissa which corresponds to the vibrational quantum number for dissociation. The area under the curve is the dissociation energy, D_0. This method gives a linear plot when the anharmonicity is small or taken into account. Otherwise a curve should be used to obtain the best approximation since a linear plot tends to overestimate the dissociation energy (see Figure 13.27).

EXAMPLE 13.10 In the ultraviolet spectrum of molecular oxygen, the Schumann–Runge bands correspond to the transition $^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$. The ground state dissociates into two ground-state oxygen atoms (^{3}P) and the excited state dissociates into one ^{3}P and one ^{1}D. This ^{1}D level lies 190 kJ mol^{-1} above the ground state. The wave numbers, ν, for absorption from the ground vibrational level v'' to the v'^{th} vibrational level of the excited state are given. From the data given, determine the dissociation energy of molecular oxygen in the ground state and in its excited state.

v'	$\tilde{\nu}$, cm^{-1}	$\Delta\tilde{\nu}$, cm^{-1}	v'	$\tilde{\nu}$, cm^{-1}	$\Delta\tilde{\nu}$, cm^{-1}
1	50 062.6 $\tilde{\nu}_1$		9	54 641.8	
		662.8 $\Delta\tilde{\nu}_1$			436.4
2	50 725.4		10	55 078.2	
		643.6 $\Delta\tilde{\nu}_2$			381.6
3	51 369.0		11	55 460.0	
		619.6 $\Delta\tilde{\nu}_3$			343.6
4	52 988.6		12	55 803.1	
		590.4			303.7
5	52 579.0		13	56 107.3	
		564.4			253.0
6	53 143.4		14	56 360.3	
		533.5			210.3
7	53 676.9		15	56 570.6	
		500.1			
8	54 177.0				
		464.8			

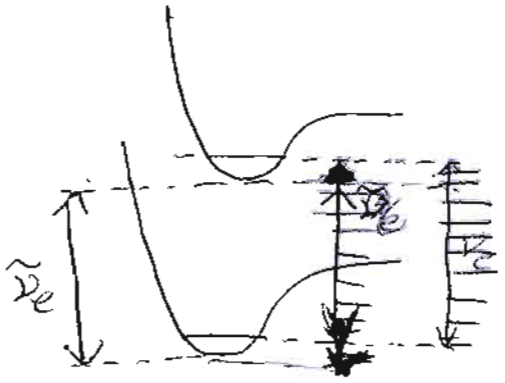
excitations

$$^3\Sigma_u^-(v') \leftarrow {}^3\Sigma_g^-(v''=0)$$

dissociation $\Rightarrow$ anharmonic oscillator terms

$$G'' = \tilde{\nu}_0''\left[(v''+\tfrac{1}{2}) - x_e''(v''+\tfrac{1}{2})^2\right]$$

$$= \tilde{\nu}_0''\left(\tfrac{1}{2} - \tfrac{1}{4}x_e''\right) \qquad v''=0$$



excited state

$$G' = \tilde{\nu}_e + \tilde{\nu}_0'\left[(v'+\tfrac{1}{2}) - x_e(v'+\tfrac{1}{2})^2\right]$$

$$\tilde{\nu}_{v'} = G' - G''$$

$$= \underline{\tilde{\nu}_e} + \tilde{\nu}_0'\left[(v'+\tfrac{1}{2}) - x_e\overbrace{(v'+\tfrac{1}{2})^2}^{v'^2+v'+\frac{1}{4}}\right] - \underline{\tilde{\nu}_0''\left(\tfrac{1}{2}-\tfrac{1}{4}x_e''\right)}$$

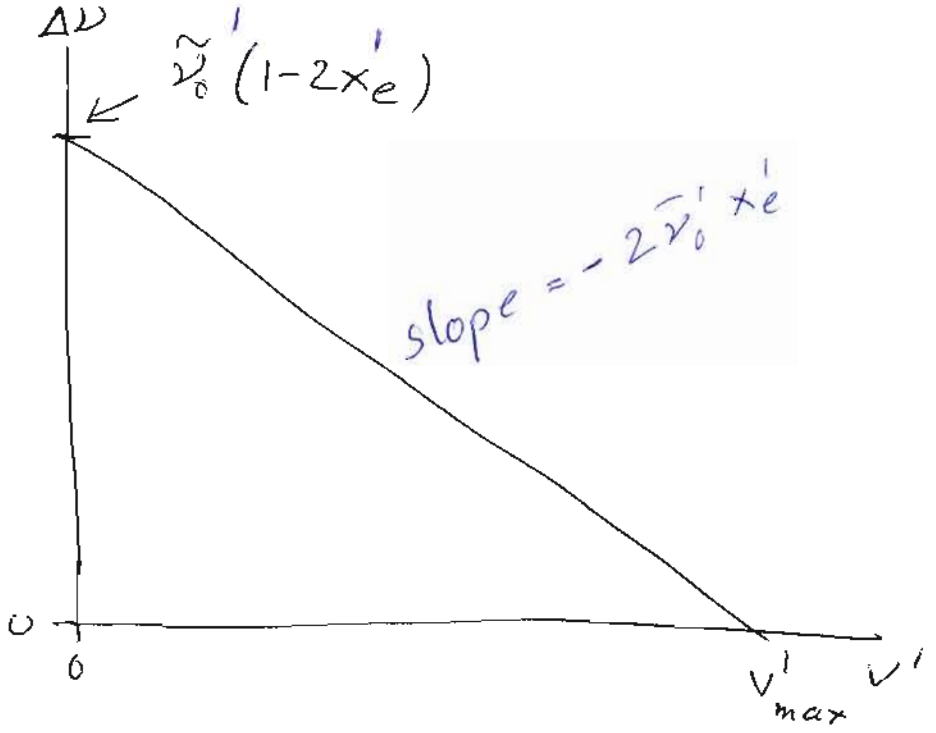
$$\Delta\tilde{\nu} = \tilde{\nu}_{v+1} - \tilde{\nu}_v \quad \text{— cancel!}$$

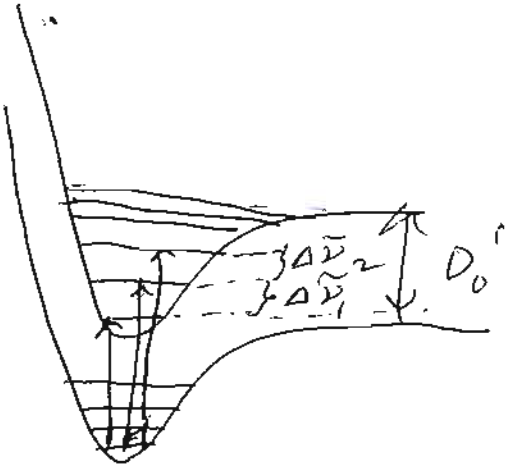
$$= \tilde{\nu}_0\Big[\underline{v'} + \tfrac{3}{2} - x_e\Big(\overbrace{(v'+1)^2}^{v'^2+2v'+1} + v' + \tfrac{5}{4}\Big)$$

$$- \underline{v'} - \tfrac{1}{2} + x_e\left(v'^2 + v' + \tfrac{1}{4}\right)\Big]$$

$$= \tilde{\nu}_0\left[1 - x_e(2v'+1+1)\right]$$

$$= \tilde{\nu}_0\left[(1-2x_e) - 2x_e v'\right]$$





$\rightarrow \sum \text{all } \Delta\tilde{\nu}_i \rightarrow D_0'$

$\sum \text{all } \Delta\tilde{\nu}_i$ = area under curve

$$\left(\int_0^{v'_{max}} \Delta\nu \, dv'\right)$$

N $(0 \to v')$ <u>absorption</u> lines:

$$\Delta\bar{\nu}_{v'} = \bar{\nu}_{v'+1} - \bar{\nu}_{v'}$$

abscissa intercept where $\Delta\bar{\nu} = 0$: v'_m

largest $v' = v'_{max}$

integer next smaller to v'_m is v'_{max}

from 5 lines

$\bar{\nu}_0''$, x_e'', $\bar{\nu}_0'$, x_e', $\bar{\nu}_e$ or $X = \bar{\nu}_0''\left(\frac{1}{2} - \frac{1}{4}x_e''\right)$

can be determined $\quad Y = \bar{\nu}_e + \bar{\nu}_0'\left(\frac{1}{2} - \frac{1}{4}x_e'\right)$

from $\bar{\nu}_{0-0}$

$$\bar{\nu}_{max} = \bar{\nu}_e + \bar{\nu}_0'\left[\left(v'_{max} + \frac{1}{2}\right) - x_e'\left(v'_{max} + \frac{1}{2}\right)^2\right]$$

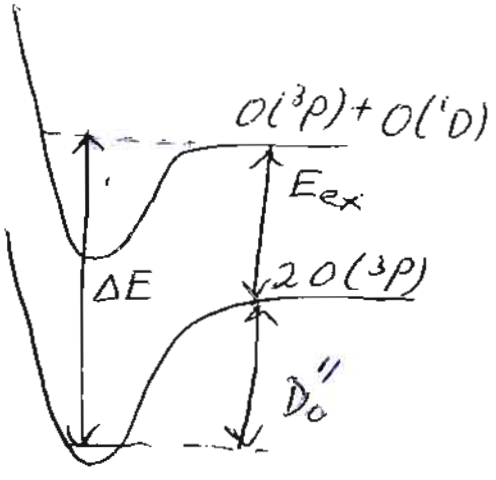
$$\tilde{\nu}_0''\left(\frac{1}{2} - \frac{1}{4}x_e''\right)$$

$$\text{area} = \sum_{v'=1}^{v'_{max}} \Delta\bar{\nu}_v = D_0'$$

$$\Delta E = hc\bar{\nu}_{max}$$

$$E_{ex} = E\left[O(^1D) - O(^3P)\right]$$

$$D_0'' + E_{ex} = \Delta E = hc\bar{\nu}_{max}$$



$\underline{O_2}$ $\Delta\bar{\nu}_1 = 662.8\ cm^{-1}$ $v' = 1$, $v'+1 = 2$

$\Delta\bar{\nu}_2 = 643.6\ cm^{-1}$ $v' = 2$, $v'+1 = 3$

$\Delta E[O(^1D) - O(^3P)] = 190\ kJ/mol$

$N_A hc\bar{\nu}_{max} = 6.21\ eV$ (31) - 12

$\Delta\bar{\nu}_1 = a + bv_1'$ $1\ eV = 96.47\ kJ/mol$

$\Delta\bar{\nu}_2 = a + bv_2'$

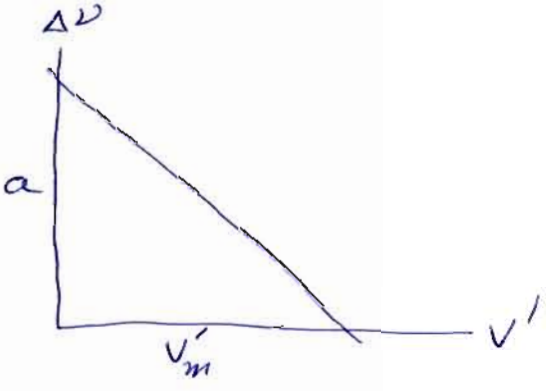
$b(v_1' - v_2') = \Delta\bar{\nu}_1 - \Delta\bar{\nu}_2$

$$b = \frac{\Delta\bar{\nu}_1 - \Delta\bar{\nu}_2}{v_1' - v_2'} = \frac{662.8 - 643.6}{1 - 2}\ cm^{-1}$$

$$= -19.2\ cm^{-1}$$

$b = -2\bar{\nu}_0' x_e'$

$\bar{\nu}_0' x_e' = 9.6\ cm^{-1}$



$\Delta\nu$ intercept:

$a = \Delta\bar{\nu}_1 - bv_1' = 662.8\ cm^2 + 19.2\ cm^{-1}$

$= \cancel{643.6\ cm^{-1}}\ 682.0\ cm^{-1}$

$\tilde{\nu}_0'(1 - 2x_e') = a$ $\bar{\nu}_0 x_e' = 9.6\ cm^{-1}$

$x_e' = \frac{9.6}{682}$

$= 0.014$

$\bar{\nu}_0' - 2\tilde{\nu}_0' x_e' = a$

$\bar{\nu}_0' - 19.2\ cm^{-1} = 682.0\ cm^{-1}$

$\bar{\nu}_0' = 701.2\ cm^{-1} \rightarrow k'$ if μ known

here: $\mu = m_O$

v' intercept

$$0 = a + b v_m'$$

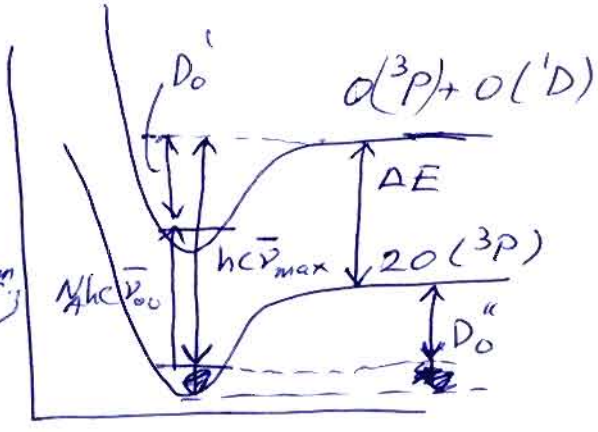
$$v_m' = -\frac{a}{b} = -\frac{682}{-19.2} = 35.5$$

$$v_{max}' = 35$$

D_0' = area under curve

$$= \frac{1}{2} \cdot a v_m' = \frac{1}{2} \cdot 682.0\,cm^{-1} \cdot 35.5$$

$$= 12106\ cm^{-1}$$



$$D_0' = N_A \cdot hc \cdot 12106\ cm^{-1}$$

$$= 6.022 \cdot 10^{23}\ mol^{-1} \cdot 6.626 \cdot 10^{-34}\ Js \cdot 2.998 \cdot 10^{10}\ \frac{cm}{s} \cdot 12106\ cm^{-1}$$

$$= \underline{D_0' = 145\ kJ/mol}$$

$$D_0'' + \Delta E = N_A hc\bar{\nu}_{max} \qquad D_0'' = N_A hc\bar{\nu}_{max} - \Delta E$$

$$N_A hc\bar{\nu}_{max} = N_A hc\bar{\nu}_{00} + D_0' \qquad = 6.21\ eV - 190\ \frac{kJ}{mol} + 145\ \frac{kJ}{mol}$$

$$1\ eV = 96.47\ kJ/mol$$

$$D_0'' = 6.21 \cdot 96.47\ kJ/mol - 190\ \frac{kJ}{mol} + 145\ \frac{kJ}{mol}$$

$$\underline{D_0'' = 554\ kJ/mol}$$

Obj Chromophores

Fate of electronically excited states

Birge-Sponer extrapolation

Transition probabilities

Chromophores

strongly absorbing groups (if they absorb in the visible, can also color a sample) are called chromophores

e.g.: C=O , C=C

CO : $n \rightarrow \pi^*$ band, maximum ~~around~~ at 285 nm

symmetry forbidden → weak

$\varepsilon \approx 10 \frac{dm^3}{mol\,cm}$

but : $\pi \rightarrow \pi^*$ band, maximum at 200 nm

allowed, very strong

$\varepsilon = 1000 - 10000 \frac{dm^3}{mol\,cm}$

also C=C : $\pi \rightarrow \pi^*$ very strong

conjugation with ~~oc~~ other double bonds brings the absorption to longer wavelengths (above: UV)

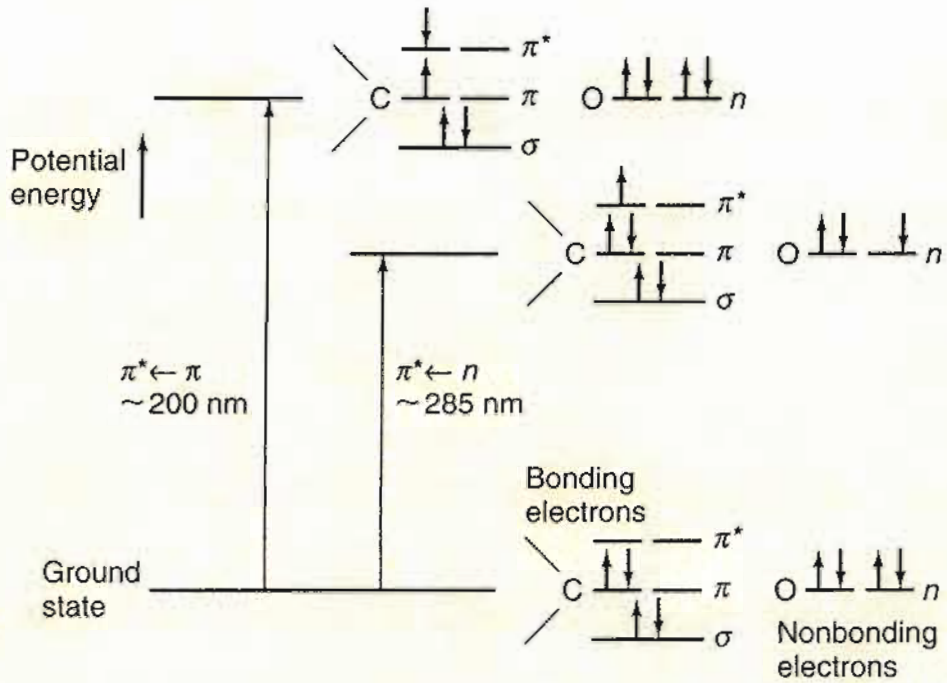


FIGURE 13.28
Two types of electronic transitions that can occur with a chromophore such as the carbonyl group.

A nonbonding (n) electron can be promoted into an empty antibonding π orbital based on carbon, and the transition marked $\pi^* \leftarrow n$ at ~285 nm is known as a $\pi^* \leftarrow n$ *transition,* read "n-to-π-star transition." Since $\pi^* \leftarrow n$ transitions are often symmetry forbidden, the absorption is weak. The more intense absorption at about 200 nm is caused by the promotion of a π electron into the antibonding π^* orbital in the electronically excited state. This is known as a $\pi^* \leftarrow \pi$ transition. This is the same mechanism responsible for the absorption found in other double bonds such as the carbon-carbon double bond, C=C.

The presence of chromophores such as the carbonyl group often causes the molecule to absorb in the visible part of the spectrum and therefore to be colored. The contribution of a particular chromophore to the absorption spectrum is considerably altered by conjugation with other chromophores. Thus, an isolated carbon-carbon

Fate of electronically excited states

an excited state can emit radiation to go to a lower state

can happen fast, if $\Delta S = 0$: fluorescence
or relatively slow, if $\Delta S \neq 0$: phosphorescence
shift to larger λ than the absorption: Stokes shift

If the exciting energy is so large, that the excitation arrives higher than ~~ds~~ diss. limit in upperstate: point a in Figure

→ dissociation: diffuse spectra

diss. within the first vibration
too short time for rotations
only at lower energy side, where no diss. happens: rot. fine structure
$1 \leftarrow 0$ absorption, $1 \rightarrow 0$ emission

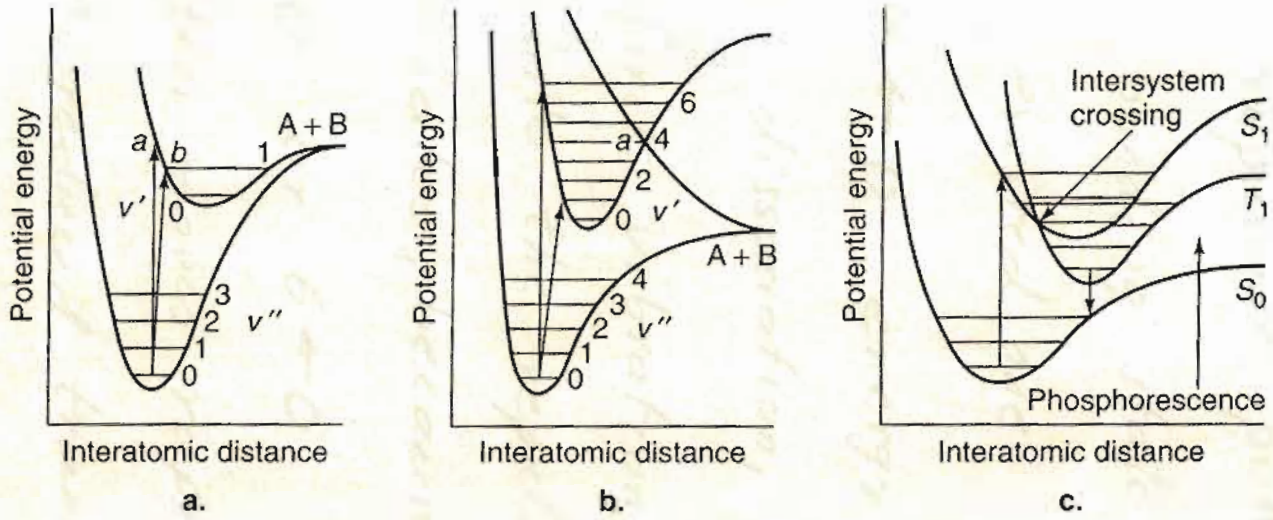


FIGURE 13.29
(a) Potential-energy curves for a diatomic molecule. The transition to point *a* leads to immediate dissociation. (b) Potential-energy curves for the case of predissociation. (c) Potential-energy curves that will lead to phosphorescence. Absorption from the singlet ground state S_0 gives the singlet excited state S_1; after a transition to the triplet state T_1, the molecule phosphoresces.

referred to as **fluorescence.**[5] This term is generally restricted to processes in which there is no change of multiplicity, in contrast to **phosphorescence** where there is a multiplicity change and in which the emission is slower. Transitions giving rise to fluorescence are included in Figure 13.25. Whereas absorption generally occurs from the ground vibrational state, fluorescent emissions often give excited vibrational states, as shown in Figure 13.25, and therefore correspond to longer wavelengths than observed in absorption. This shift to longer wavelengths is called the *Stokes shift*. Fluorescence often occurs after certain radiationless processes have occurred, and this is considered later.

The formation of an excited species can also lead to *molecular dissociation*, which can occur by different mechanisms according to the relative positions of the potential-energy curves for ground and excited states. Figures 13.29a and b relate to a diatomic molecule AB and show two situations that are of particular importance. In Figure 13.29a a *vertical* transition from the lowest vibrational level ($v'' = 0$) of the ground state takes the molecule to point *a* on the diagram. Here the energy level is higher than for A + B, and as a result the molecule dissociates in its first vibration. The spectrum corresponding to this transition

Fig. b: Predissociation

repulsive potential of a anti-bonding state crosses the upper excited one

$4 \leftarrow 0$ energy = a

dissociation, diffuse

after first vibration system goes from $v'=4$ into the repulsive state and dissociates, because crossing at turning point

$7 \leftarrow 0$ or $6 \leftarrow 0$

system moves rapidly past crossing

→ reduced transition probability into repulsive state

→ AB^* lives long enough for rotations

diffuse region around crossing

but aside from it vib./rot. bands

<u>Fig. c</u>: Triplet term crosses singlet

at turning point (slow moving) the system can cross into the triplet state (non radiationally)

$T \rightarrow S$ return to ground state delayed

$\rightarrow$ delayed emission

= phosphorescence

<u>Polyatomic molecules</u>

longer life times of excited states

reasons rearrangements necessary for return to ground state

AB^*: $\approx 10^{-13}$ s life-time

$(\text{polyatomic})^*$: up to 10^{-8} s life time

Vibrational relaxation:

collisions can lead to lower vibrational levels within the same electronic state

collisions take energy away

<u>gas phase</u>: not many collisions

→ IR emission in gas phase

Jablonski diagram: shows states and transitions

<u>Collisional quenching</u>

= external ~~quenching~~ conversion

collisions remove the energy as the system goes into lower electronically excited state

→ energy released as heat

<u>Internal quenching</u> = internal conversion

electronic energy goes into vibrations of the molecule itself:

self quenching

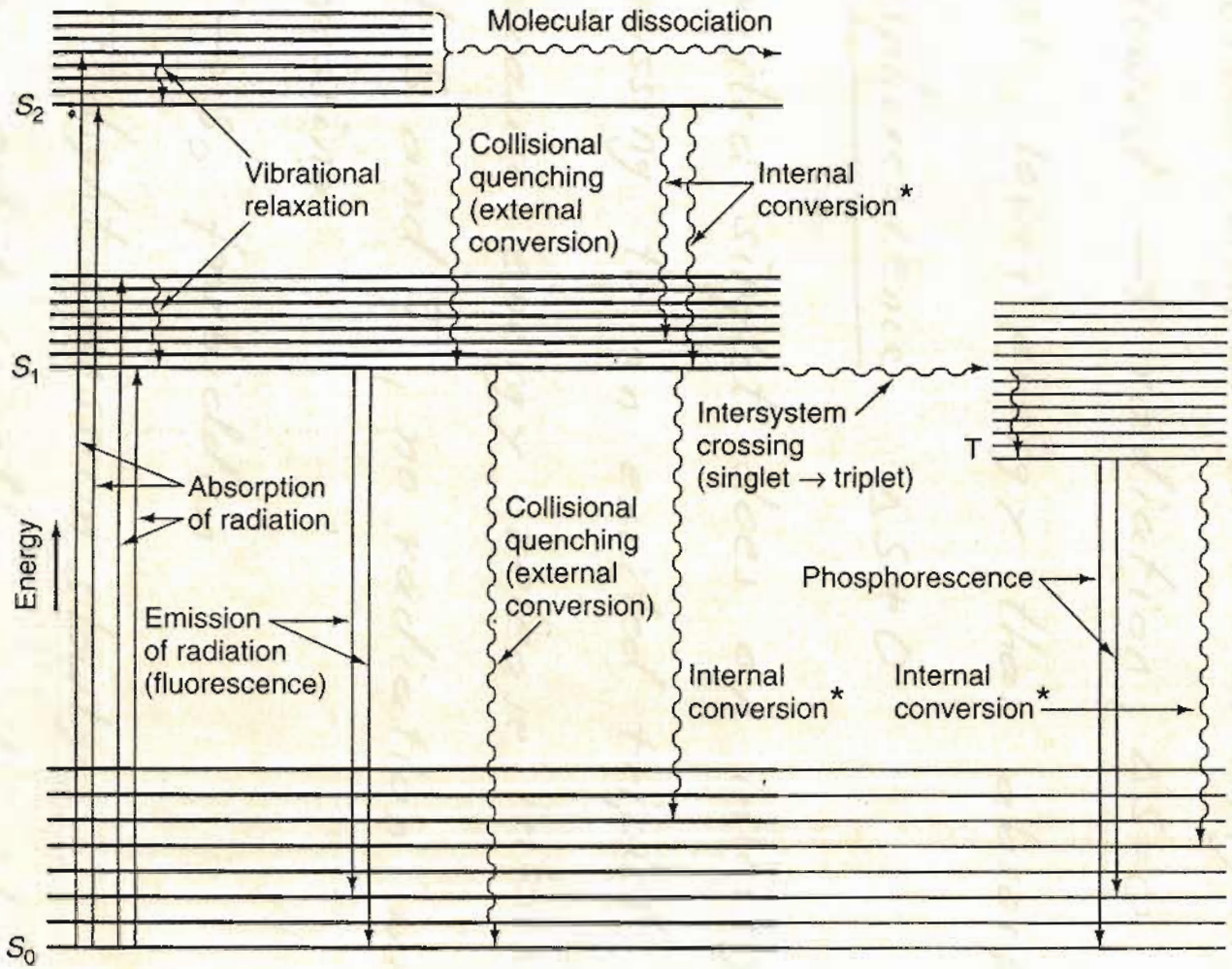


FIGURE 13.30
A Jablonski diagram, which shows the ground singlet state, S_0 two excited singlet states S_1 and S_2, and a triplet state, T. Various possible processes are represented. The internal conversions $S_2 \rightarrow S_1$ and $S_1 \rightarrow S_0$ are actually at the same energy because the excited states often lie within the potential energy surface of the lower energy state.

singlet state and occurs in 10^{-9}–10^{-8} s. The photon can drop to any of the vibrational levels of the ground state. This is usually a much slower process than vibrational relaxation, quenching, or internal conversion.

5. **Phosphorescence.** The term *fluorescence* is usually restricted to processes in which there is no change of multiplicity. The term *phosphorescence*

Fluorescence

excited Singlet to lower Singlet

allowed → radiation, $\Delta S = 0$

fast, lower energy than absorption

Phosphorescence $\Delta S \neq 0$

excited singlet does an intersystem crossing to an excited triplet

because energy release into vibrations of S and T, no radiation with the crossing

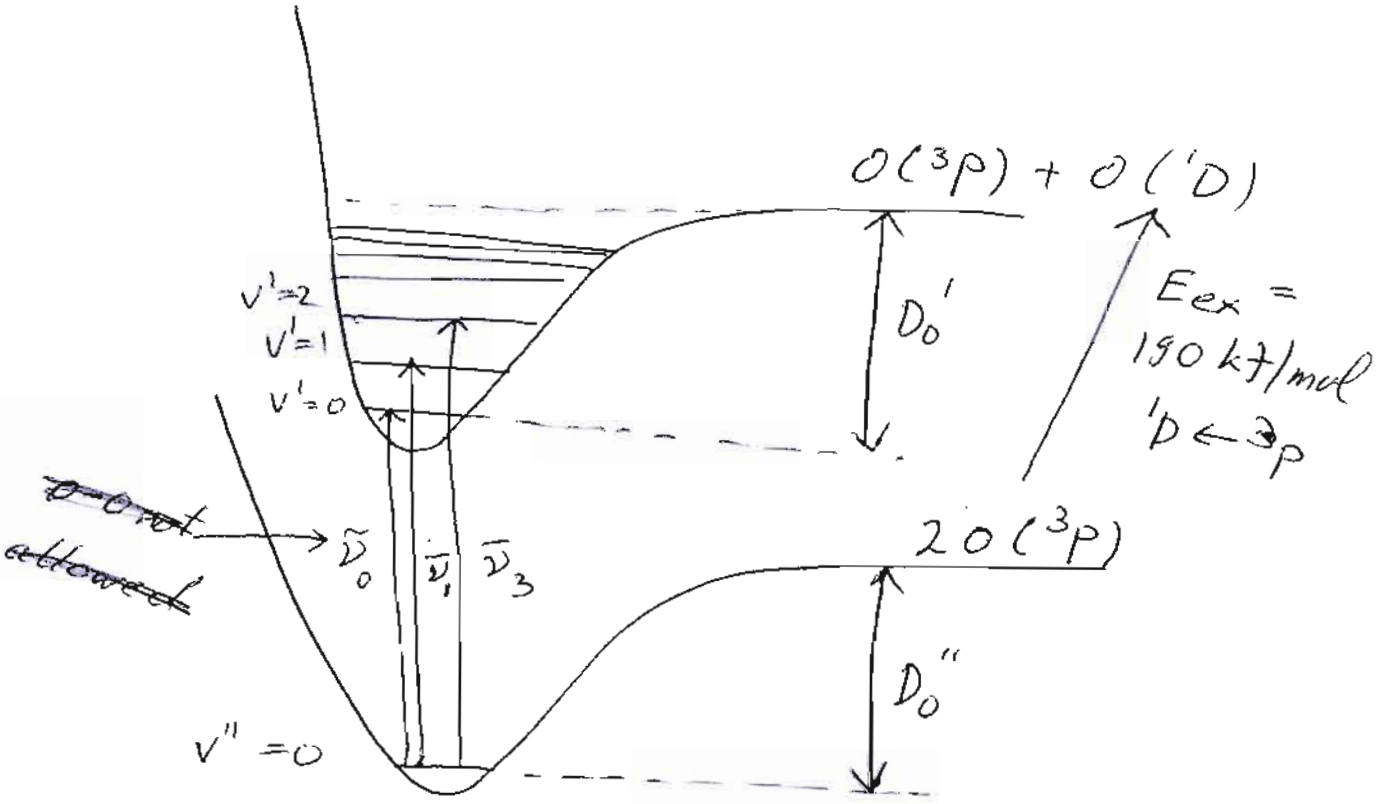
$T_1 \rightarrow S_0$ forbidden

→ light emission slowly

Spin-orbit coupling makes it possible at all.

Birge - Sponer revisited

$O_2 \quad {}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$

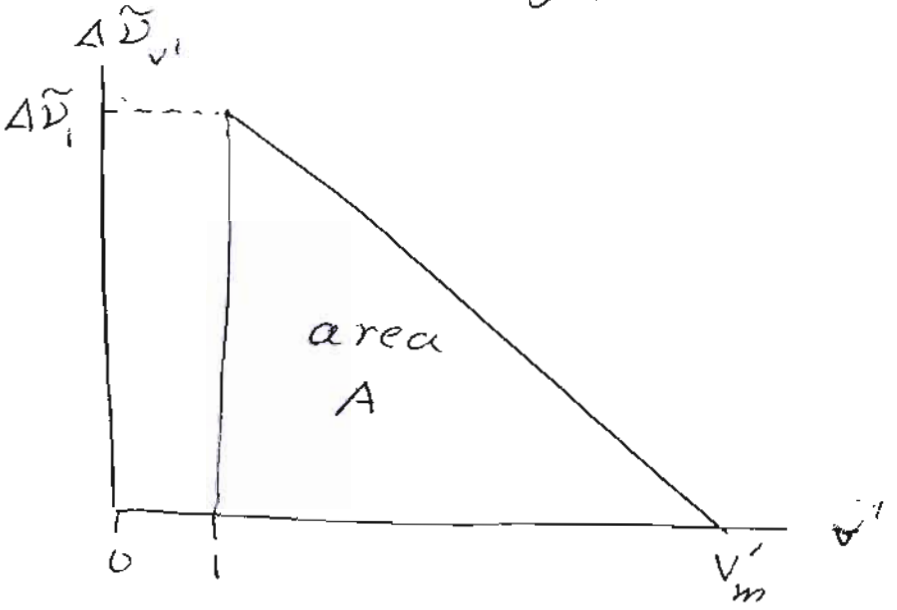


v'	$\tilde{\nu}_{v'}$ (cm⁻¹)	$\Delta\tilde{\nu}_{v'} = \tilde{\nu}_{v'+1} - \tilde{\nu}_{v'}$
1	50 062.6	
		662.8 $\Delta\tilde{\nu}_1$
2	50 725.4	
		643.6 $\Delta\tilde{\nu}_2$
3	51 369.0	

$\Delta\tilde{\nu}_{v'}$ plotted vs v' almost linear

for strictly linear: $2\Delta\tilde{\nu}$

basically enough:



if linear:

$$\Delta\tilde{\nu}_{v'} = \Delta\tilde{\nu}_1 + \frac{\Delta\tilde{\nu}_2 - \Delta\tilde{\nu}_1}{2-1}(v'-1)$$

$$= 662.8\ \text{cm}^{-1} + \frac{643.6 - 662.8}{1}\ \text{cm}^{-1}(v'-1)$$

$$= 682.0\ \text{cm}^{-1} - 19.2\ \text{cm}^{-1}\, v'$$

$$A = \frac{1}{2}\Delta\tilde{\nu}_1 (v'_m - 1)$$

triangle!

$$v'_m: \quad \Delta\tilde{\nu}_{v'_m} = 0 = (682.0 - 19.2\, v'_m)\ \text{cm}^{-1}$$

$$\rightarrow v'_m = \frac{682.0}{19.2} = 35.5$$

$$A = \frac{1}{2} \cdot 662.8 \cdot 34.5\ \text{cm}^{-1} = 11\,433\ \text{cm}^{-1}$$

$$\tilde{D}_0'' + E_{ex} = \bar{\nu}_1 + A$$

$$\bar{\nu}_{ex} = \frac{E_{ex}}{N_A hc} = \frac{190\,kJ/mol}{N_A hc} = 15900\,cm^{-1}$$

$$\tilde{D}_0'' = \bar{\nu}_1 + A - \bar{\nu}_{ex}$$

$$= (50\,062.6 + 11433 - 15900)\,cm^{-1} = 45\,596\,cm^{-1}$$

$$D_0'' = \tilde{D}_0'' \underbrace{hc}_{\frac{cm}{s}} N_A \longrightarrow kJ/mol$$

$$\bar{\nu}_0 + \tilde{D}_0' = \tilde{D}_0'' + E_{ex}$$

$$\Delta\bar{\nu}_0 = 682.0\,cm^{-1} = \bar{\nu}_1 - \bar{\nu}_0$$

from linear extrapolation before

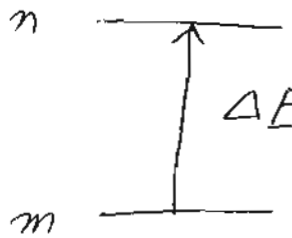
$$\longrightarrow \bar{\nu}_0 = 49\,381\,cm^{-1}$$

$$\tilde{D}_0' = \tilde{D}_0'' + \bar{\nu}_{ex} - \bar{\nu}_0$$

$$= (45596 + 15900 - 49381)\,cm^{-1}$$

$$= 12\,115\,cm^{-1}$$

Transition probabilities



$$\Delta E_{mn} = E_n - E_m$$

$$\nu_{mn} = \frac{\Delta E_{mn}}{h}$$

N_{mn}: number of transitions from m to n

$\sim$ population of m:

and $w(\nu_{mn})$ spectral energy density

$$\rightarrow \quad N_{mn} = B_{mn} N_m w(\nu_{mn})$$

B_{mn}: Einstein transition probability for absorption

spontaneous emission: $N_{nm}^{sp} = A_{nm} N_n$

$\hookrightarrow$ no need for stimulating light

$\rightarrow$ now

A_{nm}: Einstein probability for spont. emission

stimulated emission

(e.g. in Laser)

light $\nu_{mn} = \nu_{nm}$ causes emission

$$N_{nm}^{stim} = B_{nm} N_n \, w(\nu_{mn})$$

↳ population of n by absorption

total: $N_{nm} = N_n \left[A_{nm} + B_{nm} \, w(\nu_{mn}) \right]$

steady state: $N_{nm} = N_{mn}$

$B_{nm} = B_{mn}$ holds true

$$N_m B_{mn} \, w(\nu_{mn}) = N_n \left[A_{nm} + B_{mn} \, w(\nu_{mn}) \right]$$

Boltzmann distribution.

$$\frac{N_n}{N_m} = e^{-\frac{h\nu_{nm}}{k_B T}}$$

$$\rightarrow e^{-\frac{h\nu_{mn}}{k_B T}} = \frac{B_{mn} \, w(\nu_{mn})}{A_{nm} + B_{mn} \, w(\nu_{mn})}$$

Planck:

32-12

$$W(\nu_{mn}) = \frac{8\pi h \nu_{mn}^3}{c^3} \frac{1}{e^{\frac{h\nu_{mn}}{k_B T}} - 1}$$

$$e^{\frac{h\nu_{mn}}{k_B T}} = \frac{8\pi h \nu_{mn}^3}{c^3 W(\nu_{mn})} + 1$$

$$e^{-\frac{h\nu_{mn}}{k_B T}} = \frac{B_{mn} W(\nu_{mn})}{A_{mn} + B_{mn} W(\nu_{mn})}$$

$$\frac{A_{mn}}{B_{mn} W(\nu_{mn})} + 1 = \frac{8\pi h \nu_{mn}^3}{c^3 W(\nu_{mn})} + 1$$

$$\frac{A_{mn}}{B_{mn}} = \frac{8\pi h \nu_{mn}^3}{c^3}$$

Review

(probably I cannot finish all)

Absorbance: $A = \log_{10} \frac{I_0}{I}$

I_0: incident intensity

I: intensity after pass ~~of~~ through the sample

Transmittance: $T = \frac{I}{I_0}$

$$A = \log_{10} \frac{1}{T}$$

$$\log_{10} T\% = 2 - A \Rightarrow A = 2 - \log_{10} T\%$$

Lambert-Beer:

$$A = \varepsilon c l$$

c: concentration $\frac{mol}{L}$

l: light path in sample

ε: molar absorption coefficient $\frac{dm^3}{mol\ cm}$

atomic spectra

many e^- atoms: Coulomb and exchange interactions

$\rightarrow$ splitting of the terms

splitting also in 1e atoms (H):

spin-orbit coupling

$1s^2 2s^2 2p^2$: only unpaired $2p^2$ play a role for angular momentum

paired ones cancel

$l_1 = 1,\ l_2 = 1$

$\rightarrow$ $\uparrow\downarrow$ $L=0$ $\quad$ l_1 $\uparrow$ $\nearrow$ l_2 $L=1$ $\quad$ $\uparrow\uparrow$ $L=2$

	S	P	D
spins:		$\uparrow\downarrow$ $S=0$ (1/2)	$\uparrow\uparrow$ $S=1$ (1/2)
multiplicity		$2S+1=1$	$2S+1=3$

$\rightarrow$ terms: $^1S,\ ^3S,\ ^1P,\ ^3P,\ ^1D,\ ^3D$

spin-orbit coupling

ie $j = l \pm s$

$$\left.\begin{array}{l} p: l=1 \\ \text{spins}: s=\frac{1}{2} \end{array}\right\} j = \frac{1}{2}, \frac{3}{2} \quad \underline{\text{split}}!$$

Zeeman effect

levels get split in magnetic fields:

$$\Delta E = \mu_B B \rightarrow \text{magnetic flux density}$$

μ_B: Bohr's magneton

separation between neighboring lines

$$\mu_B = \frac{eh}{4\pi m_e} = 9.274 \cdot 10^{-24}\, Am^2$$

Rotational spectra

for rot. spectrum molecule must have a permanent el. dipole moment

$$E_J = J(J+1)\frac{\hbar^2}{2I} = J(J+1)\, h\, B$$

B: rotational constant (Hz)

moment of inertia $I = \mu r_0^2$ diatomics

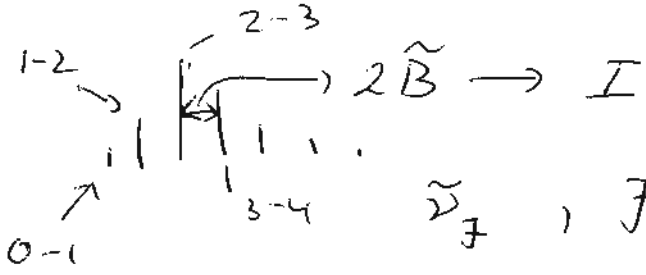
$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad c\tilde{B} = B \rightarrow Hz = s^{-1}$$

$\tilde{B} \rightarrow cm^{-1}$

$$\tilde{B} = \frac{h}{8\pi^2 I c}$$

$$\tilde{\nu}_J = \frac{E_{J+1} - E_J}{hc} = 2(J+1)\tilde{B}$$

$$\Delta J = \pm 1$$



$\tilde{\nu}_J$, $J = 0, 1, \ldots$

$$r_e = \sqrt{\frac{I}{\mu}}$$

relative intensities:

$$\frac{I_J}{I_0} = \frac{N_J}{N_0} = (2J+1)e^{-\frac{hc\tilde{B}}{k_B T} J(J+1)}$$

Rotational-vibrational spectra

$$\Delta V = \pm 1 \ , \ \Delta J = \pm 1$$

$$E_{VJ} = (V + \tfrac{1}{2})h\nu_0 + hBJ(J+1)$$

$$\tilde{\nu} = \frac{E_{1,J''\pm 1} - E_{0,J''}}{hc}$$

R-branch

$$\tilde{\nu} = \tilde{\nu}_0 + 2(J''+1)\tilde{B} \qquad \Delta J = +1$$

P-branch

$$\tilde{\nu} = \tilde{\nu}_0 - 2J''\tilde{B} \qquad J'' = 1, 2, \ldots \qquad \Delta J = -1$$

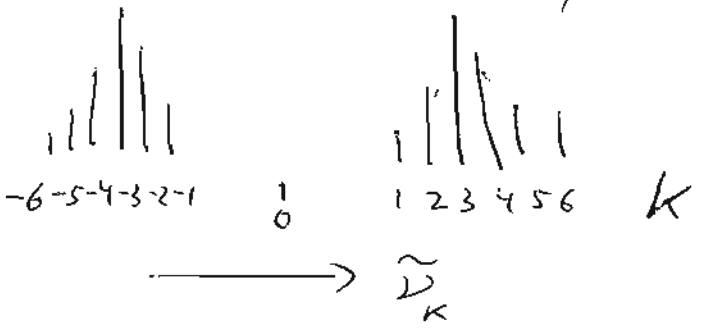
Q-branch

$$\Delta J = 0 \qquad \tilde{\nu} = \tilde{\nu}_0$$

mostly forbidden, sometimes present

$$\tilde{\nu}_k = \tilde{\nu}_0 + 2k\tilde{B} \qquad k = \pm 1, \pm 2$$

no Q-branch



relative Intensities

$$\sim \frac{N_{J''}}{N_0} = (2J''+1)e^{-\frac{hc\tilde{B}}{k_BT}J''(J''+1)}$$

$\underline{\tilde{B}}$: $\quad 4\tilde{B} = |\tilde{\nu}_1 - \tilde{\nu}_{-1}|$

$$2\tilde{B} = |\tilde{\nu}_{k+1} - \tilde{\nu}_k|$$

$\tilde{\nu}_0$: $\tilde{\nu}_0 = \frac{1}{2}(\tilde{\nu}_1 + \tilde{\nu}_{-1})$

$$\tilde{\nu}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

anharmonic terms:

$$G = \tilde{\nu}_0\left[(v+\tfrac{1}{2}) - x_e(v+\tfrac{1}{2})^2\right]$$

$\Delta V = \pm 1, \pm 2, \pm 3 \ldots$ in anharmonic oscillators

fundamental : $\tilde{\nu}_1 = \tilde{\nu}_0(1-2x_e)$

1. overtone : $\tilde{\nu}_2 = 2\tilde{\nu}_0(1-3x_e)$

$$\frac{\tilde{\nu}_1}{\tilde{\nu}_2} = \frac{1}{2}\,\frac{1-2x_e}{1-3x_e} \longrightarrow x_e$$

$$\tilde{\nu}_0 = \frac{\tilde{\nu}_1}{1-2x_e} \quad \text{or} \quad \tilde{\nu}_0 = \frac{\tilde{\nu}_2}{2(1-3x_e)}$$

2. overtone : $\tilde{\nu}_3 = 3\tilde{\nu}_0(1-4x_e)$

first hot band ($T > 500K$)

$$\tilde{\nu}_{2\leftarrow 1} = \tilde{\nu}_0(1-4x_e)$$

normal modes

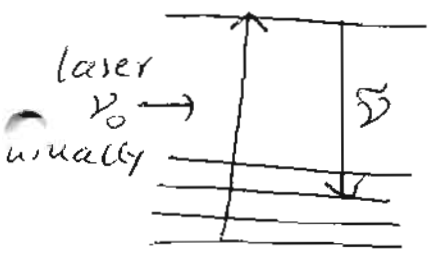
collective motions, each with own $\tilde{\nu}_0$

selection rule

for vibr. IR-spectrum: vibration must lead to an oscillating dipole moment

- the symmetry class of the normal mode must have x, y, or z in the character table to be IR active

Raman spectra



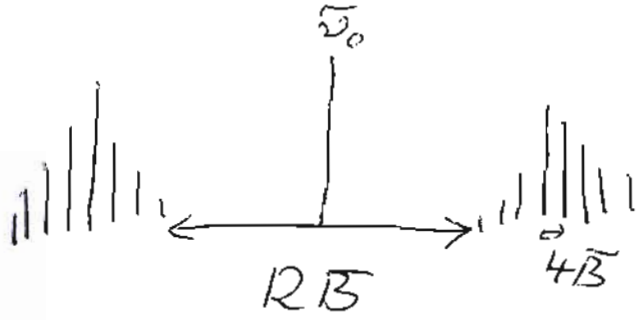
virtual level

$\tilde{\nu} < \tilde{\nu}_0$ Stokes scattering

$\tilde{\nu} > \tilde{\nu}_0$ anti-Stokes scattering

$\tilde{\nu} = \tilde{\nu}_0$ Rayleigh scattering

$\Delta V = 1, 2, \ldots \quad \Delta J = \pm 2$



Raman spectra have Q-branch

selection rule:

vibration must yield an oscillating polarizability

also H_2, O_2 have rot. Raman spectrum although no permanent dipole moments

normal modes:

symmetry class must have x^2, y^2, z^2, xy, xz, or yz for Raman activity

<u>examples for electr. transitions</u>

O_2 ground state dissociation energy

$$D_0'' = 5.09 \text{ eV}$$

ground state $^3\Sigma_g^-$

$$1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J} = 96.47 \text{ kJ/mol}$$

$$= 23.06 \text{ kcal/mol}$$

excited state: $^3\Sigma_u^-$

$$^3\Sigma_u^- \; v'=0 \leftarrow v''=0 \; ^3\Sigma_g^- : 6.21 \text{ eV}$$

potentials: minima at same r_0

or $0 \rightarrow 0$ not possible

dissociations:

$$^3\Sigma_g^- \rightarrow 2O(^3P)$$

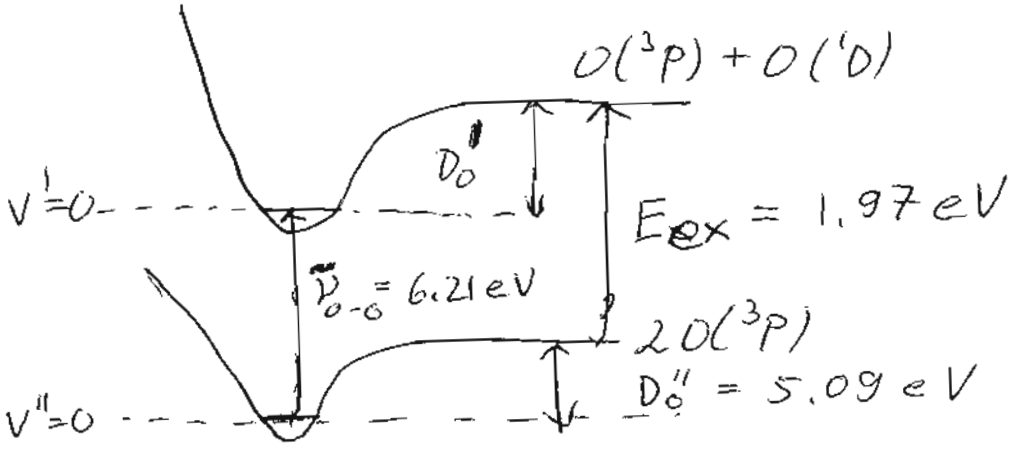
$$^3\Sigma_u^- \rightarrow O(^3P) + O(^1D)$$

$O(^1D) \leftarrow O(^3P)$: $E_{ex} = 1.97\ eV$

dissociation energy for $^3\Sigma_u^- \rightarrow O(^3P) + O(^1D)$:

$$D_0' = ?$$

soln.: sketch potentials



$$\rightarrow E(0\leftarrow 0) + D_0' = D_0'' + E_{ex}$$

$$D_0' = D_0'' + E_{ex} - E(0\leftarrow 0)$$

$$= (5.09 + 1.97 - 6.21)\ eV$$

$$= 0.85\ eV$$

groundstate: NO: $X^2\Pi$

$D_0'' = 6.6$ eV

$B^2\Pi$ $v'=0 \leftarrow v''=0$ $X^2\Pi$ $E(0\text{-}0) = 5.7$ eV

0-0: $\Rightarrow$ pot. minima at same r_0

$NO(X^2\Pi) \rightarrow N(^4S) + O(^3P)$

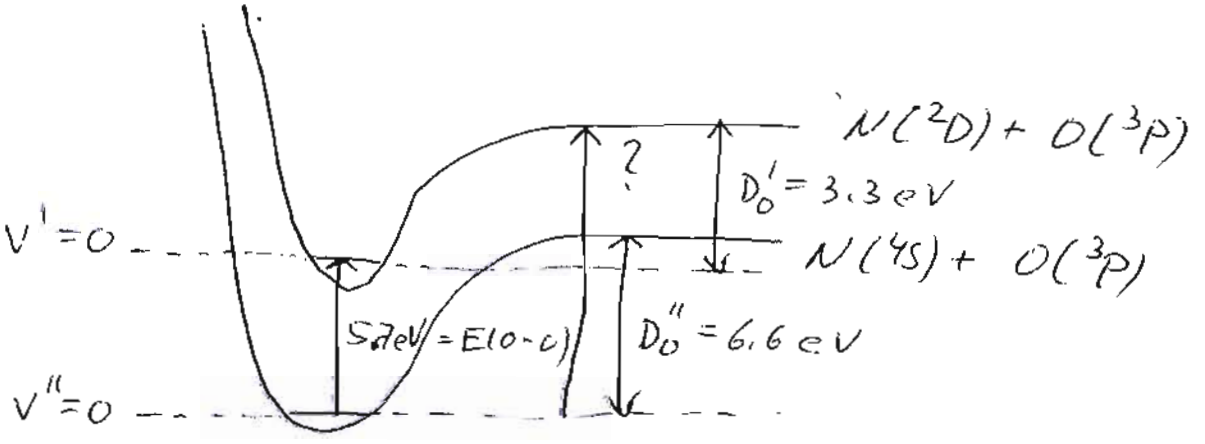
$NO(B^2\Pi) \rightarrow N(^2D) + O(^3P)$

$D_0' = 3.3$ eV

$v''=0 \rightarrow v'=0 = 5.7$ eV

$D_0'' = 6.6$ eV

$\rightarrow N(^4S) + O(^3P)$ must be <u>higher</u> than $B^2\Pi, v'=0$



diss energy $X^2\Pi \rightarrow N(^2D) + O(^3P)$?

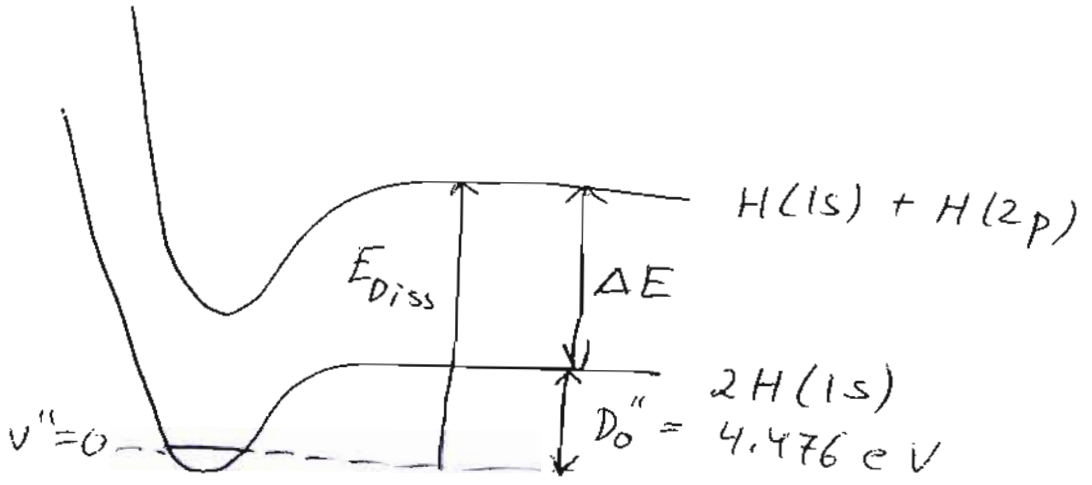
$\rightarrow E_{Diss.} = E(0\text{-}0) + D_0'$

$= (5.7 + 3.3)$ eV

$= 9.0$ eV

The dissociation energy of ground-state $H_2(g)$ into $2H(1s)$ is $4.476\ eV = D_0''$ (33) - 11

what is the dissociation energy of the ground state $H_2(g)$ into $H(1s) + H(2p)$ E_{Diss}



ΔE ~~fo~~ from Bohr's model,

because it is the energy $n=1 \rightarrow n=2$

$$\Delta E_{nm} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \qquad n < m$$

$$\Delta E = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = R\left(1 - \frac{1}{4}\right) = \frac{3}{4}R$$

Rydberg constant $R = 13.5\ eV$

$$\rightarrow \Delta E = 10.13\ eV$$

$$E_{Diss} = D_0'' + \Delta E = (4.476 + 10.13)\ eV = 14.6\ eV$$

$H_2(g) + h\nu \rightarrow H(1s) + H(2p)$

with photons $h\nu = 15\,eV$

$\rightarrow$ rest energy $\Delta = 15\,eV - 14.6\,eV$

$= 0.4\,eV$

the rest energy goes equally distributed into E_k of the H atoms

$\rightarrow$ each H gets $0.2\,eV$

$\Rightarrow 0.2\,eV = \frac{1}{2} m_H v^2$

$\rightarrow$ final speed of the H-atoms:

$$v = \sqrt{\frac{2 \cdot 0.2\,eV}{m_H}}$$