

(6)

⇒ considers this in construction of
LCAOs ⇒ symmetry-adapted linear
combinations (SALCs)

same applies to selection rules:

$$M_{21i} = -e \int \psi_f^* \hat{z} \psi_i dz$$

unchanged
by any symmetry operation

Spectroscopy

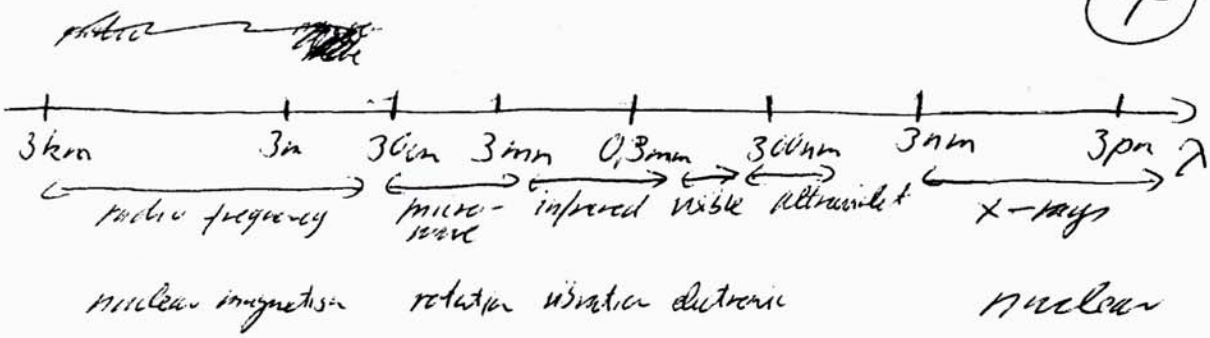
spectral lines: absorption, emission, or
scattering of photons when the
energy of a molecule changes

frequency ω , wavelength λ , wavenumber $\bar{\omega}$

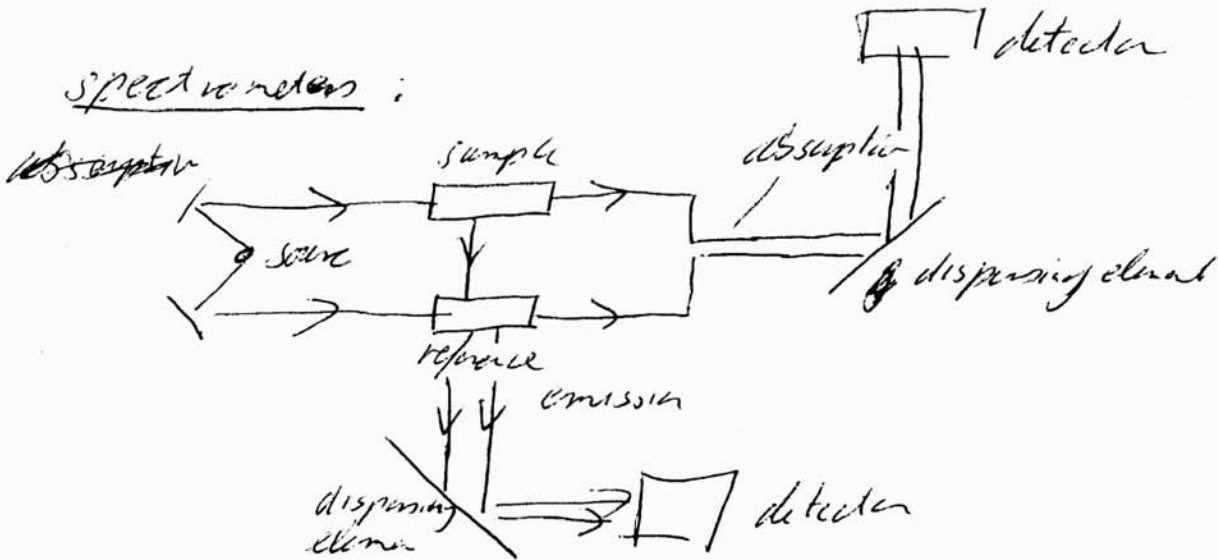
$$\lambda = \frac{c}{\omega} \quad \bar{\omega} = \frac{\omega}{c}$$

emission — spectroscopy
absorption —

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spectrometers:



Source:

- lamps: tungsten, quartz-tungsten-halogen
- gas discharge lamps: Xenon, Mercury, Deuterium
- lasers: + OPOs, tapered fibers, Ti:Sapphire-lasers

dispersive element:

separates radiation into different frequencies

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diffraction grating

$$m\lambda = d(\sin\theta - \sin\phi)$$

spacing of grating

\uparrow \uparrow \uparrow
 order angle of incidence angle of emergence

+ slit \Rightarrow monochromator

or Fourier transformation:

use Michelson interferometer with path difference p

$$J(p, \tilde{\nu}) d\tilde{\nu} = J(\tilde{\nu}) (1 + \cos 2\pi \tilde{\nu} p) d\tilde{\nu}$$

\uparrow
Fourier transform

$$\Rightarrow J(p) = \int_0^{\infty} J(p, \tilde{\nu}) d\tilde{\nu} = \int_0^{\infty} J(\tilde{\nu}) (1 + \cos 2\pi \tilde{\nu} p) d\tilde{\nu}$$

$$\Rightarrow \boxed{J(\tilde{\nu}) = 4 \int_0^{\infty} \left\{ \frac{1}{2} J(p) - \frac{1}{2} J(0) \right\} \cos 2\pi \tilde{\nu} p dp}$$

Detectors:

- photomultiplier (PMT): tube or photo diode
- charge-coupled device (CCD)
- mercury-cadmium-telluride (MCT) - detector

Intensities of spectral lines

$T = \frac{J}{J_0}$
transmitted / incident

Beer - Lambert law:

$J = J_0 10^{-\epsilon c_j l}$

- ϵ : molar absorption coefficient
- l : length of sample
- c_j : molar concentration

Absorption intensities: (\rightarrow Einstein)

stimulated absorption $w = B \rho$

w : rate of change of probability of the molecule being forced in the upper state

B : Einstein coefficient

$\rho d\nu$: energy density of radiation in the frequency range ν to $\nu + d\nu$

stimulated emission: $w' = B' \rho$ - Einstein coeff. of stimulated emission

+ spontaneous emission:

total rate of transition from the upper to the lower state:

$w' = A + B' \rho$

Einstein coeff. of spontaneous emission

$B = B'$

$A = \left(\frac{8\pi h \nu^3}{c^3} \right) B$

$$\vec{\mu}_{fi} = \langle f | \vec{\mu} | i \rangle = \int \psi_f^* \vec{\mu} \psi_i d\tau$$

electric dipole moment
operator

for the molecule to be able to interact with the EM-field and absorb or create a photon of frequency ω , it must possess, at least transiently, a dipole oscillating at that frequency.

$$B = \frac{1/\epsilon_0 \mu_0^2}{6\epsilon_0 \hbar^2}$$

Justification 16.3

We know from the Boltzmann distribution (Section 2.1) that the probability that a gas molecule of mass m and speed s in a sample with temperature T has kinetic energy $E_k = \frac{1}{2}ms^2$ is proportional to $e^{-ms^2/2kT}$. The observed frequencies, ν_{obs} , emitted or absorbed by the molecule are related to its speed by eqn 23:

$$\nu_{\text{obs}} = \nu \left(\frac{1}{1 \pm s/c} \right)$$

where ν is the unshifted frequency. When $s \ll c$, the Doppler shift in the frequency is

$$\nu_{\text{obs}} - \nu \approx \pm \nu s/c$$

which implies a symmetrical distribution of observed frequencies with respect to molecular speeds. More specifically, the intensity I of a transition at ν_{obs} is proportional to the probability of finding the molecule that emits or absorbs at ν_{obs} , so it follows from the Boltzmann distribution and the expression for the Doppler shift that

$$I(\nu_{\text{obs}}) \propto e^{-m c^2 (\nu_{\text{obs}} - \nu)^2 / 2kT}$$

which has the form of a Gaussian function. The width at half-height can be calculated directly from the exponent (see the *Maths commentary*) to give eqn 24.

(b) Lifetime broadening

It is found that spectroscopic lines from gas-phase samples are not infinitely sharp even when Doppler broadening has been largely eliminated by working at low temperatures. The same is true of the spectra of samples in condensed phases and solution. This residual broadening is due to quantum mechanical effects. Specifically, when the Schrödinger equation is solved for a system that is changing with time, it is found that it is impossible to specify the energy levels exactly. If on average a system survives in a state for a time τ (tau), the lifetime of the state, then its energy levels are blurred to an extent of order δE , where

$$\delta E \approx \frac{\hbar}{\tau} \quad (16.25)$$

This expression is reminiscent of the Heisenberg uncertainty principle (eqn 11.46), and consequently this **lifetime broadening** is often called 'uncertainty broadening'. When the energy spread is expressed as a wavenumber through $\delta E = \hbar c \delta \tilde{\nu}$, and the values of the fundamental constants introduced, this relation becomes

$$\delta \tilde{\nu} \approx \frac{5.3 \text{ cm}^{-1}}{\tau/\text{ps}} \quad (16.26)$$

No excited state has an infinite lifetime; therefore, all states are subject to some lifetime broadening and, the shorter the lifetimes of the states involved in a transition, the broader the corresponding spectral lines.

Two processes are responsible for the finite lifetimes of excited states. The dominant one for low-frequency transitions is **collisional deactivation**, which arises from collisions between molecules or with the walls of the container. If the **collisional lifetime**, the mean time between collisions, is τ_{col} , the resulting collisional

Spectroscopy, electronic transitions

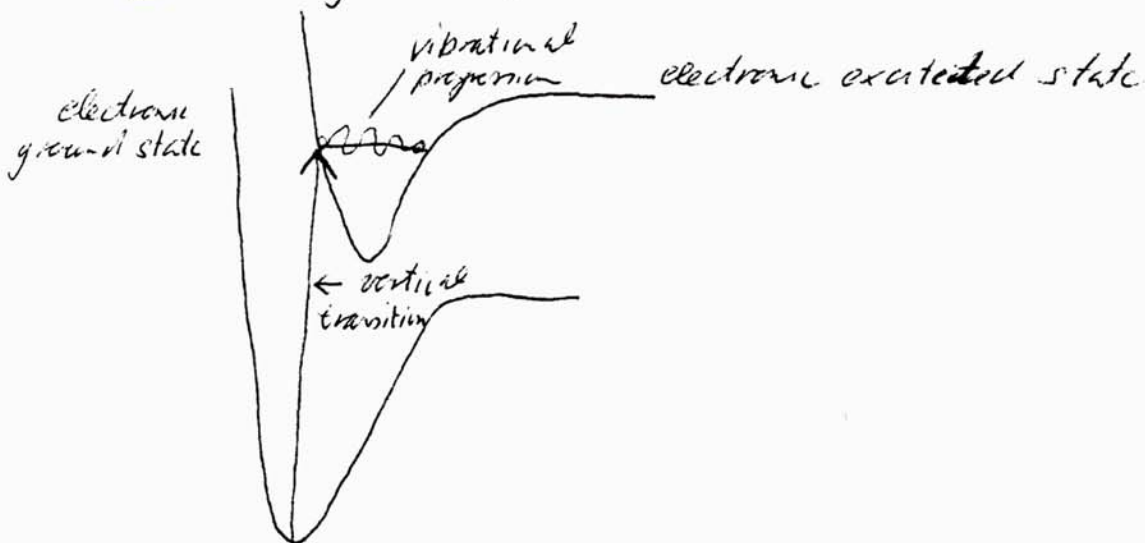
no simple analytic expressions for the electronic energy levels of molecules!



⇒ The only allowed transitions are transitions that are accompanied by a change of parity

Frank-Condon principle:

Because the nuclei are so much more massive than the electrons, an electronic transition takes place very much faster than the nuclei can respond.



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charge-transfer transitions:

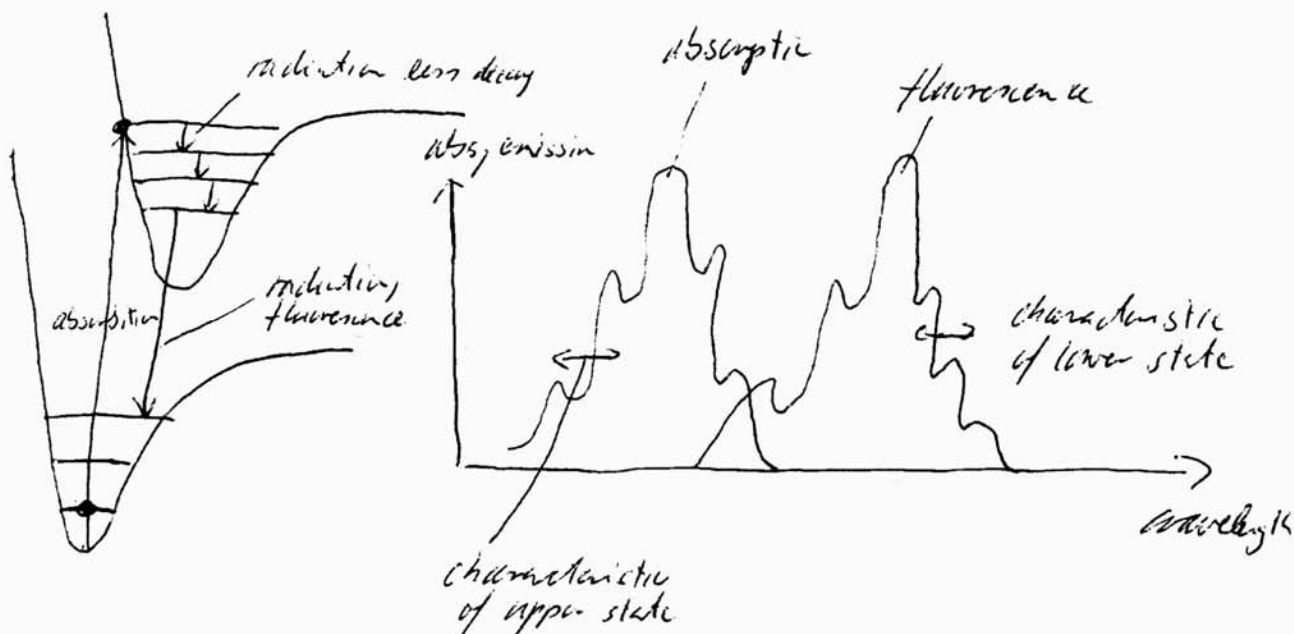
- a complex may absorb radiation as a result of the transfer of an electron from the ligands into the d-orbitals of the central atom or vice versa
- electron moves through a considerable distance, which means that the transition dipole moment may be large \Rightarrow absorption is intense

fates of electronically excited states:

radiative decay process \Rightarrow photon

nonradiative \Rightarrow vibration, rotation, translation

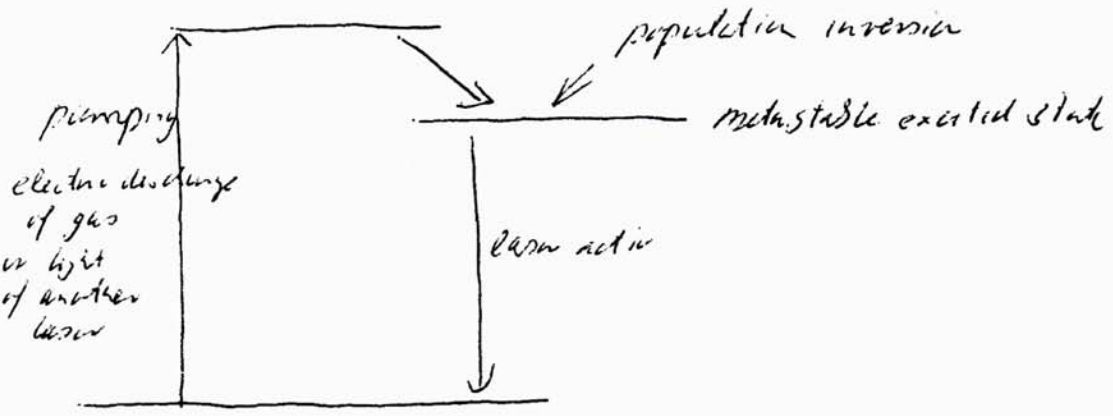
Fluorescence



phosphorescence: the same + intersystem crossing

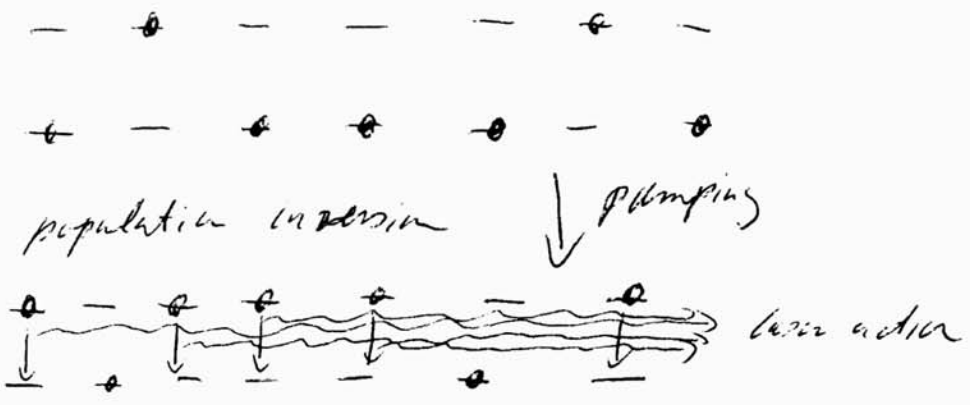
Lasers (\rightarrow Einstein)

general principles:



3-level laser

thermal equilibrium



Cavity:

length of cavity

two mirrors \Rightarrow interference $n \cdot \frac{1}{2} \lambda = L$

+ interference compatible with laser medium

\Rightarrow resonant modes

• light parallel to cavity, low divergence

• coherence: spatial coherence = in phase across the cross-section

coherence length \leftarrow temporal coherence = in phase along the beam

coherence length l_c

$$l_c = \frac{\lambda^2}{2\Delta\lambda}$$

$\Delta\lambda$: range of wavelengths present in the beam

light bulb: $l_c = 400 \mu\text{m}$

He-Ne laser: $\Delta\lambda = 2 \mu\text{m}$ $l_c = 10 \text{cm}$

Q-switching:

laser can operate $\left\{ \begin{array}{l} \text{continuously CW} \\ \text{pulsed PW} \end{array} \right.$

power concentrated into a brief pulse

\Rightarrow Q-switching:

- achieve a population inversion in the absence of the resonant cavity
- plunge the population-inverted medium into cavity

\Rightarrow into gate Pockels cell in laser cavity

Pockels cell converts plane-polarized light to circularly polarized light when an electrical potential difference is applied \rightarrow re-stimulated emission

Mode-locking:

- ⇒ picosecond pulses
- resonant modes differ in frequency by multiples of $\frac{c}{2L}$
- lock phases of resonant modes
 - ⇒ sharp peaks, picosecond bursts
- achieved by varying the Q-factor of the cavity periodically at the frequency $\frac{c}{2L}$

resonant modes

$$E_n(t) = E_0 e^{2\pi i(\nu + \frac{nc}{2L})t}$$

$$E(t) = \sum_n E_n(t) = E_0 e^{2\pi i \nu t} \sum_{n=0}^{N-1} e^{i\pi nct/L}$$

$$= E_0 e^{2\pi i \nu t} \frac{\sin \frac{N\pi ct}{2L}}{\sin \frac{\pi ct}{2L}} \cdot e^{(N-1)i\pi ct/2L}$$

$$\Rightarrow I \sim E_0^2 \frac{\sin^2 \frac{N\pi ct}{2L}}{\sin^2 \frac{\pi ct}{2L}}$$

⇒ pulses with maxima separated by $t = \frac{2L}{c}$

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Laser types:

1. Solid-State laser active medium is a crystal or a glass

- Nd-YAG - Laser

Nd³⁺ in yttrium aluminium garnet

$$\lambda = 1064 \text{ nm}$$

- titanium sapphire laser

Ti³⁺-ions in a crystal of sapphire (Al₂O₃)

pumped by Nd-YAG laser

$$\lambda = 700 \text{ nm} - 1000 \text{ nm} \quad \text{fibronic laser}$$

/ at 500 nm
broad absorption band that
arises from intrinsically allowed
d-d transitions

- laser diodes!

2. Gas laser

- helium-neon lasers (ratio 5:1)

excitation of He-atom by electric discharge
⇒ He-Ne collision transfer of energy to Ne

- argon-ion laser

- krypton-ion laser

3) Chemical and excimer lasers

4) Dye lasers

fiber lasers

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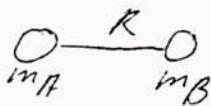
Pure rotation spectra

①

moment of inertia $J = \sum m_i r_i^2$

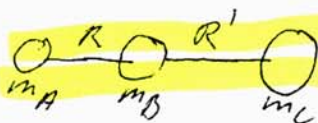
types of molecules:

• diatomics

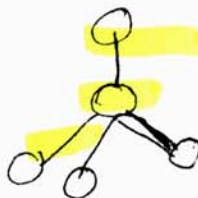


$$J = \frac{m_A m_B}{m_A + m_B} R^2$$

• linear rotors



• spherical rotors



• symmetric rotors

• asymmetric rotors

$$\Rightarrow E = \frac{1}{2} J_a \omega_a^2 + \frac{1}{2} J_b \omega_b^2 + \frac{1}{2} J_c \omega_c^2 = \frac{J_a^2}{2J_a} + \frac{J_b^2}{2J_b} + \frac{J_c^2}{2J_c}$$

angular momentum $J_a = J_a \omega_a$

spherical rotors:

$$E = \frac{J^2}{2J} = J(J+1) \frac{\hbar^2}{2J} \quad J = 0, 1, 2, \dots$$

$$= hc B J(J+1)$$

$$B = \frac{\hbar}{4\pi c J} \quad \text{rotational constant}$$

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Symmetric rotors

e.g. CH_3Cl or NH_3

$$E = hc F(J, K)$$

$$F(J, K) = B J(J+1) + (A-B)K^2 \quad J = 0, 1, 2, \dots$$

$$K = 0, \pm 1, \pm 2, \dots$$

$$A = \frac{h}{4\pi c I_B} \quad B = \frac{h}{4\pi c I_A}$$

Linear rotor and the Stark effect

$$E(J, M_J) = hc B J(J+1) + a(J, M_J) \mu^2 E^2$$

$$\text{with } a(J, M_J) = \frac{J(J+1) - 3M_J^2}{2hc B J(J+1)(2J-1)(2J+3)}$$

μ : electric dipole moment

Diatomic molecules and centrifugal distortion

$$E = hc F(J)$$

$$F(J) = B J(J+1) - D_J J^2(J+1)^2$$

\uparrow
centrifugal distortion constant

$$D_J \approx \frac{4B^3}{\omega^2}$$

Rotational rules and transitions

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$$\Delta J = \pm 1 \quad \Delta M_J = 0, \pm 1$$

for diatomic molecules:

$$\Psi_{\text{total}} = \Psi_{\text{e.m}} \Psi_{\text{vib}}$$

$$\Psi = \underbrace{|\epsilon\rangle}_{\text{electrons}} \underbrace{|\nu\rangle}_{\text{vibrational}} \underbrace{Y_{JM_J}(\theta, \phi)}_{\substack{\text{spherical harmonics} \\ \text{for rotation}}}$$

\Rightarrow transition dipole moment:

$$\begin{aligned} \vec{\mu}_{fi} &= \langle \epsilon_f \nu_f Y_{J_f M_{J_f}} | \vec{\mu} | \epsilon_i \nu_i Y_{J_i M_{J_i}} \rangle \\ &= \langle Y_{J_f M_{J_f}} | \vec{\mu}_{\text{eol}} | Y_{J_i M_{J_i}} \rangle \end{aligned}$$

$$\mu_{\text{eol},x} = \mu_0 \sin\theta \cos\phi$$

$$\mu_{\text{eol},y} = \mu_0 \sin\theta \sin\phi$$

$$\mu_{\text{eol},z} = \mu_0 \cos\theta$$

$$\Rightarrow \mu_{fi,z} \sim \langle Y_{J_f M_{J_f}} | Y_{1,0} | Y_{J_i M_{J_i}} \rangle \neq 0$$

$$\text{for } J_f - J_i = \pm 1 \quad M_{J_f} - M_{J_i} = 0$$

$$\mu_{fi,x} \neq 0$$

$$\mu_{fi,y} \neq 0$$

$$\Rightarrow \begin{aligned} J_f - J_i &= \pm 1 \\ M_{J_f} - M_{J_i} &= \pm 1 \end{aligned}$$

Rotational Raman spectra

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In addition to permanent dipole induced dipole:

$$\mu = \alpha E$$

↑
polarizability

// for rotational Raman transitions the molecule must be anisotropically polarizable.

e.g. diatomic molecules

$$\mu_{ind} = \alpha E(t) = \alpha E \cos \omega_i t$$

molecule rotates with ω_R

$$\Rightarrow \alpha = \alpha_0 + \Delta\alpha \cos 2\omega_R t$$

$$\text{with } \Delta\alpha = \alpha_{||} - \alpha_{\perp} \neq 0 \cong \text{anisotropic}$$

$$\mu_{ind} = \underbrace{\alpha_0 E \cos \omega_i t}_{\text{Rayleigh}} + \frac{1}{2} E \Delta\alpha \left\{ \cos(\omega_i + 2\omega_R) + \cos(\omega_i - 2\omega_R) \right\}$$

Raman lines

selection rules:

linear rotors: $\Delta J = 0, \pm 2$

Symmetric rotors: $\Delta J = 0, \pm 1, \pm 2$ $\Delta K = 0$

spherical rotors: no anisotropic polarizability

non-spherical rotors: anisotropic polarizability

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Linear rotor:

$\Delta J = +2 \Rightarrow$ higher rotational state,
wavenumber of the incident radiation
is decreased

\Rightarrow Stokes lines

$$\tilde{\nu} = \tilde{\nu}_i - 2B(2J+3) \quad J=0, 1, 2$$

$\Delta J = -2 \Rightarrow$ anti-Stokes lines

$$\tilde{\nu} = \tilde{\nu}_i + 2B(2J-1) \quad J=2, 3, 4$$

Vibrations of diatomic molecules

molecular potential energy

$$V(x) = V(0) + \frac{dV}{dx}\bigg|_0 x + \frac{1}{2} \frac{d^2V}{dx^2}\bigg|_0 x^2 + \dots$$

$x = R - R_e$ ≈ 0 ≈ 0
just offset at minimum

$$\approx \frac{1}{2} \frac{d^2V}{dx^2}\bigg|_0 x^2 = \frac{1}{2} k x^2$$

$\underbrace{\hspace{1.5cm}}_{=k}$

$$\Rightarrow \frac{\hbar^2}{2m_{eff}} \frac{d^2\psi}{dx^2} + \frac{1}{2} k x^2 \psi = E \psi$$

with $m_{eff} = \frac{m_1 m_2}{m_1 + m_2}$

$$E_0 = (\nu + 1/2) h \omega \quad \omega = \sqrt{\frac{k}{m_{eff}}} \quad \nu = 0, 1, 2$$

$$= hc G(\nu) \quad G(\nu) = (\nu + 1/2) \tilde{\nu}$$

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_{eff}}}$$

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selection rules

• infrared active:

the electric dipole moment of the molecule must change when the atoms are displaced relative to one another

• $\Delta l = \pm 1$

• for diatomic molecule:

transition dipole moment $\langle \psi_+ | \vec{\mu} | \psi_i \rangle$

2 partial charges $\pm \delta q$ separated by a distance $R = R_0 + x$

$$\Rightarrow \mu = R \delta q = R_0 \delta q + x \delta q = \mu_0 + x \delta q$$

↑
dipole moment when
molecules have their equilibrium

$$\langle \psi_+ | \vec{\mu} | \psi_i \rangle = \mu_0 \langle \psi_+ | \psi_i \rangle + \delta q \langle \psi_+ | x | \psi_i \rangle$$

$$\begin{aligned} \delta q &= \frac{d\mu}{dx} \\ &= \langle \psi_+ | x | \psi_i \rangle \frac{d\mu}{dx} \end{aligned}$$

↑ must be unequal zero

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Anharmonicity:

- vibrational terms are only approximate because they are based on a parabolic approximation

- Morse potential energy

$$V = hc D_e \left\{ 1 - e^{-a(r-R_e)} \right\}^2 \quad a = \sqrt{\frac{m\omega^2}{2hcD_e}}$$

|
depth of the potential minimum

$$E_v = hc G(v)$$

$$\text{with } G(v) = \left(v + \frac{1}{2}\right) \tilde{\nu} - \left(v + \frac{1}{2}\right)^2 x_e \tilde{\nu}$$

$$x_e = \frac{a^2 \tilde{h}}{2m\omega^2} = \frac{\tilde{\nu}}{4D_e} \quad \text{anharmonicity constant}$$

Vibration - rotation spectra

Just as ice-skaters rotate more rapidly when they bring their arms in, and more slowly when they throw them out, so the molecular rotation is either accelerated or retarded by a vibrational transition.

⇒ rotational transitions accompanying the vibrational transitions

⇒ band spectra: large number of closely spaced components

Vibrational Raman spectra of diatomic molecules.

selection rule: polarizability should change as the molecules vibrate

$\Delta v = \pm 1$ + Stokes line
 - Anti-Stokes line

applies to homo- and heteronuclear diatomic molecules

Justification:

$$\mu_{fi} = \langle \psi_f | \alpha | \psi_i \rangle E = \langle \psi_f | \alpha(x) | \psi_i \rangle E$$

$$\alpha(x) = \langle E | \alpha | E \rangle$$

small displacements from the equilibrium bond length

$$\mu_{fi} = \langle \psi_f | \alpha(0) + \frac{d\alpha}{dx} \Big|_0 x + \dots | \psi_i \rangle E =$$

$$\underbrace{\langle \psi_f | \psi_i \rangle}_{=0} \alpha(0) E + \frac{d\alpha}{dx} \Big|_0 \langle \psi_f | x | \psi_i \rangle E + \dots$$

$$\neq 0 \text{ if Raman active}$$

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Vibrations of polyatomic molecules

polyatomic molecules have several modes of vibration, spectra very complex

normal modes:

nonlinear molecule: $3N - 6$ modes
linear molecule: $3N - 5$ modes

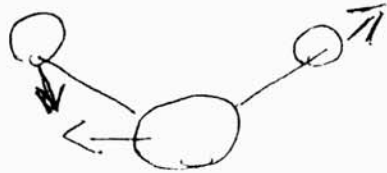


1.

e.g. H_2O



2.



3.

Note: • Vibrational spectroscopy of

biological also

• binding of protein cannot be

detected by optical microscopy

⇒ combine with vibrational spectroscopy

⇒ vibrational microscopy, Raman microscopy

infrared spectroscopy, SERS,

resonance Raman spectroscopy

infrared absorption spectra of polyatomic molecules:

motion corresponding to a normal mode should be accompanied by a change of dipole moment.

Vibrational Raman spectra:

normal modes are Raman active if they are accompanied by a changing polarizability

Resonance Raman spectra

= using incident radiation that nearly coincides with the frequency of an electronic transition of the molecule

⇒ much greater intensity
spectrum is simplified

Coherent anti-Stokes Raman spectroscopy
(CARS)

2 lasers beams of frequencies ω_1 and ω_2
pass through sample

\Rightarrow mix together, ~~cause~~ cause coherent radiation

$$\omega_3 = 2\omega_1 - \omega_2$$

ω_2 varied until it matches any Stokes-line
such as $\omega_2 = \omega_1 - \Delta\omega$

$$\Rightarrow \omega_3 = 2\omega_1 - (\omega_1 - \Delta\omega) = \omega_1 + \Delta\omega$$

\uparrow
ant-stokes line

\Rightarrow narrow beam of
high intensity

\Rightarrow suppresses incoherent
background radiation