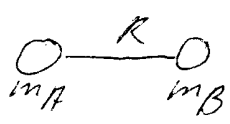


# Pure rotation spectra

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

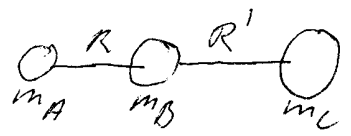
types of molecules:

• diatomics

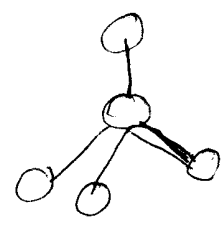


$$I = \frac{m_A m_B}{m_A + m_B} R^2$$

• linear rotors



• spherical rotors



• symmetric rotors

• asymmetric rotors

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

angular momenta  $J_a = I_a \omega_a$

spherical rotors:

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

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

$B = \frac{\hbar}{4\pi c I}$  rotational constant

Symmetric rotors

e.g. CH<sub>3</sub>Cl or NH<sub>3</sub>

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

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

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

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

Linear rotor and the Stark effect

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

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

$\mu$ : electric dipole moment

Diatomic molecules and centrifugal distortion

$$E = hc F(J)$$

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

↑  
centrifugal distortion constant

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

# Rotational rules and transitions

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

for diatomic molecules:

$$\Psi_{total} = \Psi_{c.m.} \Psi_{vib} \Psi_{rot}$$

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

⇒ transition dipole moment:

$$\begin{aligned} \vec{\mu}_{fi} &= \langle \epsilon_f, \nu_f, Y_{J_f, M_{J_f}} | \vec{\mu} | \epsilon_i, \nu_i, Y_{J_i, M_{J_i}} \rangle \\ &= \langle Y_{J_f, M_{J_f}} | \vec{\mu} e_{0l} | Y_{J_i, M_{J_i}} \rangle \end{aligned}$$

$$\begin{aligned} \mu_{e_{0,x}} &= \mu_0 \sin \theta \cos \phi \\ \mu_{e_{0,y}} &= \mu_0 \sin \theta \sin \phi \\ \mu_{e_{0,z}} &= \mu_0 \cos \theta \end{aligned}$$

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

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

$$\begin{aligned} \mu_{fi,x} \neq 0 \\ \mu_{fi,y} \neq 0 \end{aligned} \Rightarrow \begin{aligned} J_f - J_i &= \pm 1 \\ M_{J_f} - M_{J_i} &= \pm 1 \end{aligned}$$

# Rotational Raman spectra

(4)

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  $\omega_R$

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

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

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

Raman lines

selection rules:

$$\text{Linear rotors: } \Delta J = 0, \pm 2$$

$$\text{Symmetric rotors: } \Delta J = 0, \pm 1, \pm 2 \quad \Delta K = 0$$

spherical rotors: no anisotropic polarizability

non-spherical rotors: anisotropic polarizability

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

$$V(x) = V(0) + \underbrace{\frac{dV}{dx}}_{\approx 0 \text{ just offset}} \Big|_0 x + \frac{1}{2} \underbrace{\frac{d^2V}{dx^2}}_{=k} \Big|_0 x^2 + \dots$$

$x = R - R_e$

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

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

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

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

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

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

selection rules

• infrared active:

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

•  $\Delta \ell = \pm 1$

• for diatomic molecule:

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

2 partial charges  $\pm \delta q$  separated by a distance  $l = r_0 + x$

$$\Rightarrow \mu = l \delta q = r_0 \delta q + x \delta q = \mu_0 + x \delta q$$

↑  
dipole moment when  
nuclei have their equilibrium

$$\langle \psi_+ | \vec{\mu} | \psi_i \rangle = \mu_0 \underbrace{\langle \psi_+ | \psi_i \rangle}_{=0} + \delta q \langle \psi_+ | x | \psi_i \rangle$$

$$\delta q = \frac{d\mu}{dx} \quad \uparrow \text{ has to be unequal zero}$$

7

## Anharmonicity:

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

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

|  
depth of the potential minimum

$$E_v = hc G(v)$$

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

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

## 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

8

# Vibrational Raman spectra of diatomic molecules.

selection rule: polarizability should change as the molecules vibrate

$$\Delta v = \pm 1 \quad \begin{matrix} + & \text{Stokes line} \\ - & \text{Anti-Stokes line} \end{matrix}$$

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

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

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

$\neq 0$  if Raman active



# Vibrations of polyatomic molecules

9

polyatomic molecules have several modes of vibration, spectra very complex

normal modes:

nonlinear molecule:  $3N - 6$  modes

linear molecule:  $3N - 5$  modes

e.g.  $H_2O$

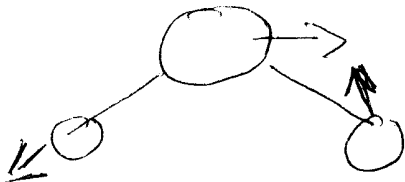
1.



2.



3.



- Note : • Vibrational spectroscopy of biological cells
  - binding of proteins 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 simpler

(11)

## Coherent anti-Stokes Raman spectroscopy

(CARS)

2 laser beams of frequencies  $\omega_1$  and  $\omega_2$  pass through sample

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

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

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

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

$\uparrow$   
anti-stokes line

$\Rightarrow$  narrow beam of  
high intensity

$\Rightarrow$  suppresses incoherent  
background radiation

# Electronic transitions, spectroscopy

13

12

electronic transitions in molecules rather complex

diatomic molecules:

even parity: orbital has the same sign under inversion

odd parity: orbital changes sign

Franck-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

