13. Molecular Spectroscopy

Microwave absorption spectroscopy
Infrared absorption spectroscopy

Classical models $\rightarrow$ normal-mode analysis, selection rule, group theory, etc.

13-1 Different Regions of the Electromagnetic Spectrum are Used to Investigate Different Molecular Processes

Region	Microwave	Far IR	Infrared	Vis-UV
ν / Hz	$10^9 \sim 10^{11}$	$10^{11} \sim 10^{13}$	$10^{13} \sim 10^{14}$	$10^{14} \sim 10^{16}$
λ / m	$0.3 \sim 3\times10^{-3}$	$3\times10^{-3} \sim 10^{-5}$	$3\times10^{-5} \sim 7\times10^{-7}$	$7\times10^{-5} \sim 2\times10^{-7}$
$\tilde{\nu}$ / cm^{-1}	$0.033 \sim 3.3$	$3.3 \sim 330$	$330 \sim 14500$	$14500 \sim 50000$
E / J molecule^{-1}	$6.6\times10^{-25} \sim$ 6.6×10^{-23}	$6.6\times10^{-23} \sim$ 6.6×10^{-21}	$6.6\times10^{-21} \sim$ 2.9×10^{-19}	$2.9\times10^{-19} \sim$ 1.0×10^{-18}
process	rotation of polynuclear molecule	rotation of small molecule	vibration of flexible molecule	electronic transition

13-2 Rotational Transitions Accompany Vibrational Transitions.

Harmonic oscillator

$$E_{\upsilon} = \left(\upsilon + \frac{1}{2}\right)h\nu \quad \upsilon = 0,1,2,\cdots$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Energy of molecular vibration

$$G(\upsilon) = \left(\upsilon + \frac{1}{2}\right)\widetilde{\nu} \quad (= E/hc)$$

Rigid rotator

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

degeneracy $\quad g_J = 2J+1$

Energy of molecular rotation

$$F(J) = \widetilde{B}J(J+1) \quad (= E_J/hc)$$

$$E_{\upsilon,J} = G(\upsilon) + F(J) = \left(\upsilon + \frac{1}{2}\right)\widetilde{\nu} + \widetilde{B}J(J+1)$$

ca. $100 \sim 1000 : 1$

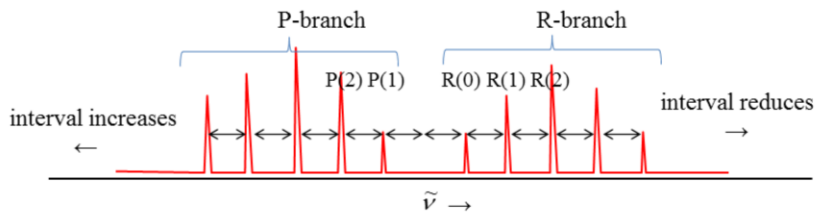## 13-2 Rotational Transitions Accompany Vibrational Transitions. (cont.)

Selection rule $\begin{cases} \Delta \upsilon = +1 \\ \Delta J = \pm 1 \end{cases}$

when $\Delta J = +1$

$$\widetilde{\nu}_{obs} = \widetilde{E}_{\upsilon+1, J+1} - \widetilde{E}_{\upsilon, J}$$
$$= \widetilde{\nu} + 2\widetilde{B}(J+1) \quad J = 0, 1, 2, \cdots \quad \text{(R-branch)}$$

when $\Delta J = -1$

$$\widetilde{\nu}_{obs} = \widetilde{E}_{\upsilon+1, J-1} - \widetilde{E}_{\upsilon, J}$$
$$= \widetilde{\nu} - 2\widetilde{B}J \quad J = 1, 2, \cdots \quad \text{(P-branch)}$$

P-branch

R-branch

P(2) P(1)   R(0) R(1) R(2)

interval increases
←

interval reduces
→

$\widetilde{\nu} \rightarrow$

13-3 Vibration-Rotation Interaction Accounts for the Unequal Spacing of the Lines in the P and R Branches of a Vibration-Rotation Spectrum

$$E_{\upsilon,J} = \left(\upsilon + \frac{1}{2}\right)\tilde{\nu} + \tilde{B}J(J+1)$$

$$\tilde{B} = \frac{h}{8\pi c\mu R_e^{\,2}}$$

R_e increases with increasing υ

$\Rightarrow B$ decreases ($B_1 < B_0$)

when $\upsilon = 0 \rightarrow 1$

$$\tilde{\nu}_R(\Delta J = +1) = \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J+1)(J+2) - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1)$$

$$= \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

$$\tilde{\nu}_P(\Delta J = -1) = \frac{3}{2}\tilde{\nu} + \tilde{B}_1(J-1)J - \frac{1}{2}\tilde{\nu} - \tilde{B}_0 J(J+1)$$

$$= \tilde{\nu} - (\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

$$\tilde{B}_\upsilon = \tilde{B}_e - \tilde{\alpha}_e\left(\upsilon + \frac{1}{2}\right)$$

For $^1\text{H}^{127}\text{I}$: $\tilde{B}_e = 6.508\,\text{cm}^{-1}$, $\tilde{\alpha}_e = 0.168\,\text{cm}^{-1}$

13-4 The Lines in a Pure Rotational Spectrum are not Equally Spaced

Molecule rotates vigorously $\Rightarrow$ bonds are lengthened ($\rightarrow I$ increases)

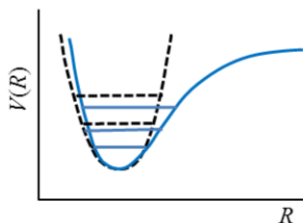$$F(J) = \widetilde{B}J(J+1) - \widetilde{D}J^2(J+1)^2$$

$$\widetilde{D}:$$
centrifugal distortion constant

$$\widetilde{\nu} = F(J+1) - F(J)$$
$$= 2\widetilde{B}(J+1) - 4\widetilde{D}(J+1)^3$$

For $^1\mathrm{H}^{35}\mathrm{Cl}$: $\quad \widetilde{B} = 10.403\,\mathrm{cm}^{-1}$ $\quad \widetilde{D} = 0.00044\,\mathrm{cm}^{-1}$

13-5 Overtones are Observed in Vibrational Spectra

$$V(R) = V(R_e) + \frac{1}{2!}\frac{d^2V}{dR^2}(R - R_e)^2 + \cdots$$

$$= \frac{k}{2}x^2 + \frac{\gamma_3}{6}x^3 + \frac{\gamma_4}{24}x^4 \cdots$$

$$G(\upsilon) = \tilde{\nu}_e\left(\upsilon + \frac{1}{2}\right) - \tilde{x}_e\tilde{\nu}_e\left(\upsilon + \frac{1}{2}\right)^2 + \cdots$$

$\tilde{x}_e(<< 1)$: anharmonicity constant

selection rule : $\Delta\upsilon = \pm1, \pm2, \pm3, \cdots$ intensity is weakened over 2nd harmonic.

$$\tilde{\nu}_{obs} = G(\upsilon) - G(0) = \tilde{\nu}_e\upsilon - \tilde{x}_e\tilde{\nu}_e\upsilon(\upsilon + 1)$$

For $^1H^{35}Cl$: $\tilde{\nu}_e = 2990.9\,cm^{-1}$, $\tilde{x}_e\tilde{\nu}_e = 52.82\,cm^{-1}$

13-6 Electronic Spectra Contain Electronic, Vibrational, and Rotational Information
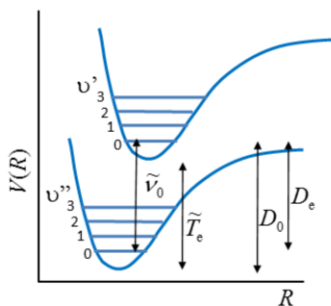
Energy gap between electronic levels $\rightarrow$ visible $\sim$ ultraviolet

Each level is accompanied by vibrational and rotational levels.

Born-Oppenheimer approximation: Electronic and rovibrational levels are independent.

$$E_{\text{total}} = \widetilde{\nu}_{\text{el}} + G(\upsilon) + F(J)$$
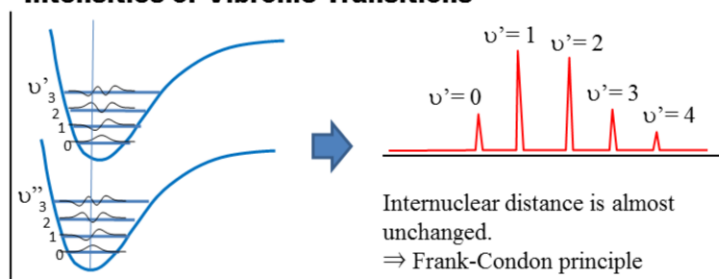
$$= \widetilde{\nu}_{\text{el}} + \left(\upsilon + \frac{1}{2}\right)\widetilde{\nu} - \widetilde{x}_e\widetilde{\nu}_e\left(\upsilon + \frac{1}{2}\right)^2 + \widetilde{B}J(J+1) - \widetilde{D}J^2(J+1)^2$$

$$\widetilde{\nu}_{\text{obs}} = \widetilde{T}_e + \left(\frac{1}{2}\widetilde{\nu}_e' - \frac{1}{4}\widetilde{x}_e'\widetilde{\nu}_e'\right) - \left(\frac{1}{2}\nu_e'' - \frac{1}{4}\widetilde{x}_e''\nu_e''\right)$$

$$+ \widetilde{\nu}_e'\upsilon' - \widetilde{x}_e'\widetilde{\nu}'\upsilon'(\upsilon'+1)$$

$$= \widetilde{\nu}_{00} + \widetilde{\nu}_e\upsilon' - \widetilde{x}_e'\widetilde{\nu}'\upsilon'(\upsilon'+1) \qquad \upsilon' = 0, 1, 2, \cdots$$

13-7 The Franck-Condon Principle Predicts the Relative Intensities of Vibronic Transitions

Internuclear distance is almost unchanged.
$\Rightarrow$ Frank-Condon principle

13-8 The Rotational Spectrum of a Polyatomic Molecule Depends Upon the Principal Moments of Inertia of the Molecule

Moment of inertia $\quad I_{xx}, I_{yy}, I_{zz}$ (moment of inertia around axes)

Product of inertia $\quad I_{xy}, I_{yz}, I_{zx}, I_{yx}, I_{zy}, I_{xz}$

$$\begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \rightarrow \begin{pmatrix} I_A & 0 & 0 \\ 0 & I_B & 0 \\ 0 & 0 & I_C \end{pmatrix}$$

Diagonalization is realized for a certain coordinate system.
$\Rightarrow$ principal moment of inertia ($I_A \leq I_B \leq I_C$)

13-8 The Rotational Spectrum of a Polyatomic Molecule Depends Upon the Principal Moments of Inertia of the Molecule. (cont.)

Rotational constants: $\tilde{A} \geq \tilde{B} \geq \tilde{C}$

$$\tilde{A} = \frac{h}{8\pi^2 c I_A}, \quad \tilde{B} = \frac{h}{8\pi^2 c I_B}, \quad \tilde{C} = \frac{h}{8\pi^2 c I_C}$$

○spherical top
$I_A = I_B = I_C$

○symmetrical top
$I_A < I_B = I_C$ (prolate)
$I_A = I_B < I_C$ (flat)

○asymmetrical top
$I_A \neq I_B \neq I_C$

Energy levels of prolate symmetric top

$$F(J,K) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$$

Energy levels of flat symmetrical top

$$F(J,K) = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2$$

$J = 0, 1, 2, \cdots$
$K = 0, \pm 1, \pm 2, \cdots \pm J$

selection rules: $\Delta J = 0, \pm 1 \ \Delta K = 0 \ (K \neq 0)$
$\Delta J = \pm 1 \ \Delta K = 0 \quad (K = 0)$

Polynuclear molecules have small stiffness.
$\Rightarrow$ large centrifugal distortion
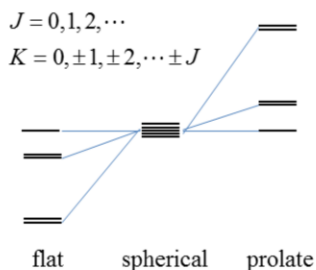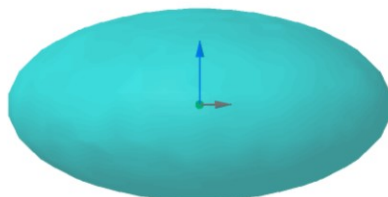
flat   spherical   prolate

13-8 The Rotational Spectrum of a Polyatomic Molecule Depends Upon the Principal Moments of Inertia of the Molecule. (cont.)

Prolate symmetrical top
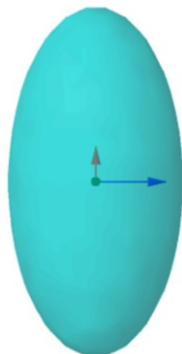
13-8 The Rotational Spectrum of a Polyatomic Molecule Depends Upon the Principal Moments of Inertia of the Molecule. (cont.)

Flat symmetrical top

Center of Mass
  4.570 3.016 5.231

Molecular Weight
  211.084

Tensor of Inertia
  1674.674 45.952   106.506
  45.952   1179.412 338.680
  106.506   338.680   678.149
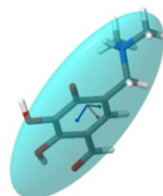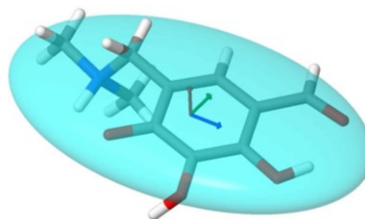
Principal Moment of Inertia
  1701.819 1327.732 502.684

Principal Axes
  0.968   0.191   0.164
  0.244 -0.876 -0.417
 -0.064 -0.443   0.894