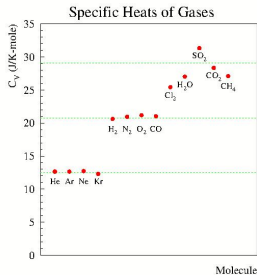
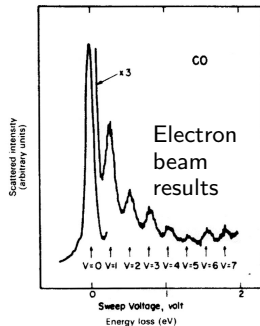
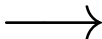
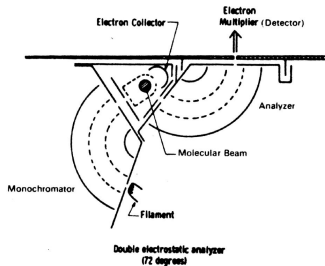
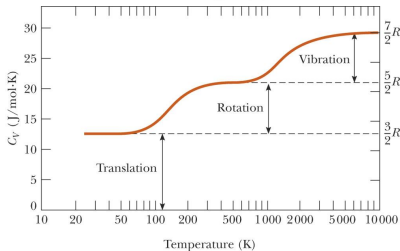
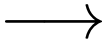
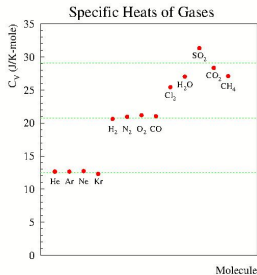
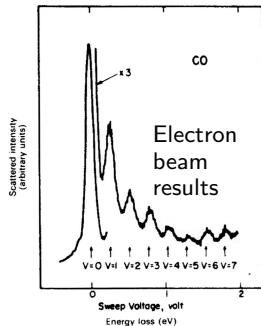


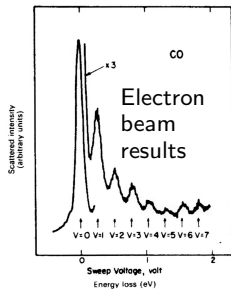
$$\Delta E = 0.25 \pm 0.05 \text{ eV}$$





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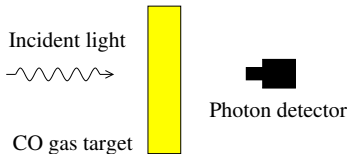


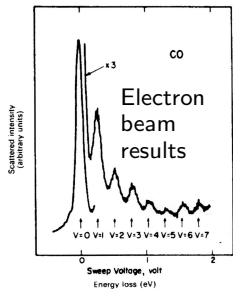


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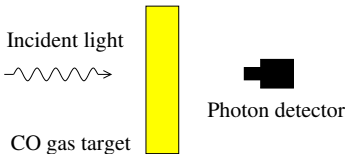
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CO Absorption Spectrum

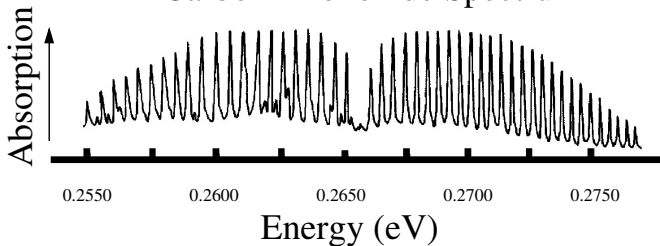




CO Absorption Spectrum



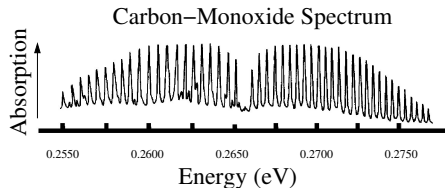
Carbon-Monoxide Spectrum



Excited states of carbon monoxide (CO) can be observed by measuring the absorption spectrum shown below. The molecule can both vibrate and rotate at the same time. The rotational energy states of a rigid rotator are

$$E_\ell = \frac{\hbar^2}{2\mathcal{I}}\ell(\ell + 1)$$

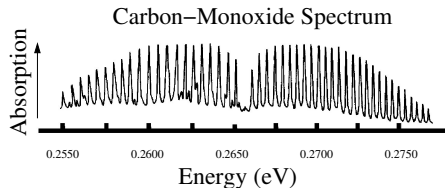
where \mathcal{I} is the moment of inertia. The vibrational part of the energy is described by the harmonic oscillator so $E_n = (n + \frac{1}{2})\hbar\omega_0$ with $\Delta E = \hbar\omega_0 = 0.25 \pm 0.05$ eV from our previous results. How do you get the expression above for the rotational energy? Is CO a rigid rotator?



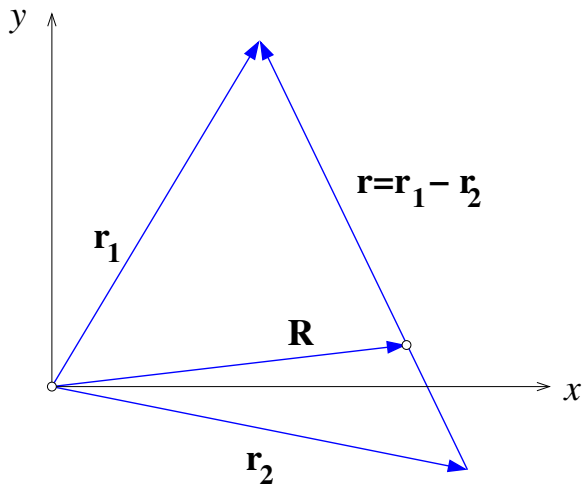
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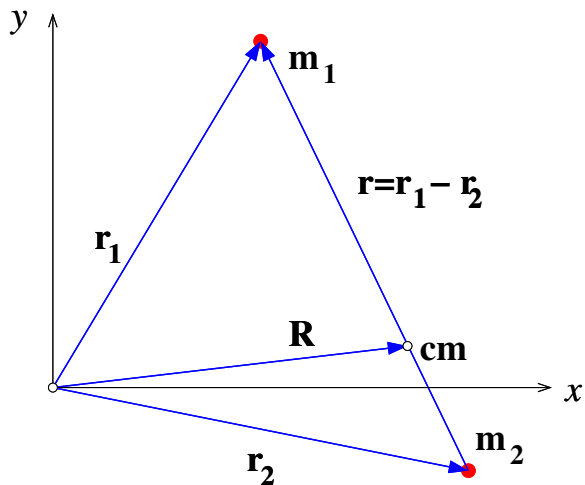
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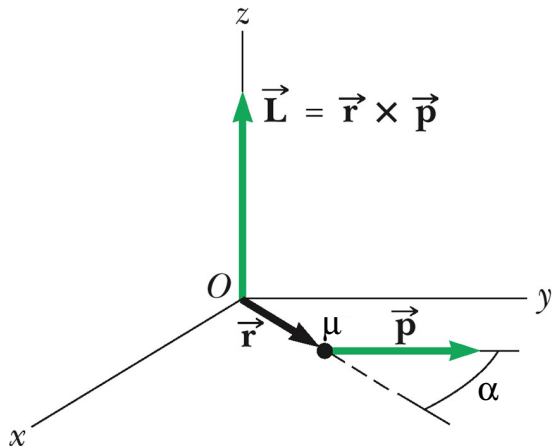
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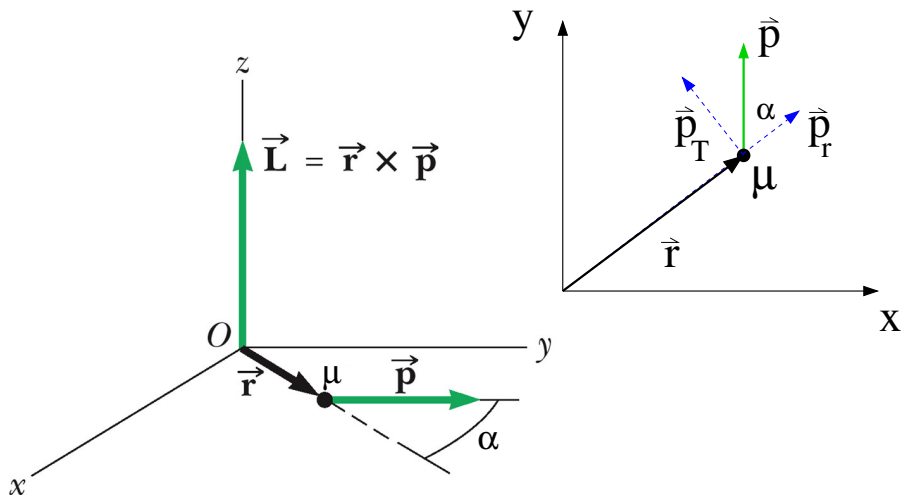


- ① What is the kinetic and potential energy between the carbon and oxygen atoms in CO in the CM frame in cartesian and spherical coordinates?
- ② How do you decompose the kinetic energy into radial and angular parts?
- ③ What is the Schroedinger equation for the rigid rotator?
- ④ What is the solution of the rigid rotator Schroedinger equation?









The Laplacian

$$\nabla^2 \psi = \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi$$

The Laplacian

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The Schroedinger Equation in 3D

$$-\frac{\hbar^2}{2\mu} \nabla^2\psi + V(r)\psi = E\psi$$

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi + V(r)\psi = E\psi$$

Steps along the way.

$$+\frac{m_\ell^2}{\sin^2 \theta} \Theta - \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) = A\Theta$$

Steps along the way.

$$+\frac{m_\ell^2}{\sin^2 \theta} \Theta - \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) = A\Theta$$

Legendre's Associated Equation

$$(1 - z^2) \frac{d^2 \Theta}{dz^2} - 2z \frac{d\Theta}{dz} + \left(A - \frac{m_\ell^2}{1 - z^2} \right) \Theta = 0 \quad \text{where} \quad z = \cos \theta$$

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And its recursion relationship when $m_\ell = 0$

$$a_{k+2} = \frac{k(k+1) - A}{(k+2)(k+1)} a_k$$

We have the recursion relationship when $m_\ell = 0$

$$a_{k+2} = \frac{k(k+1) - A}{(k+2)(k+1)} a_k$$

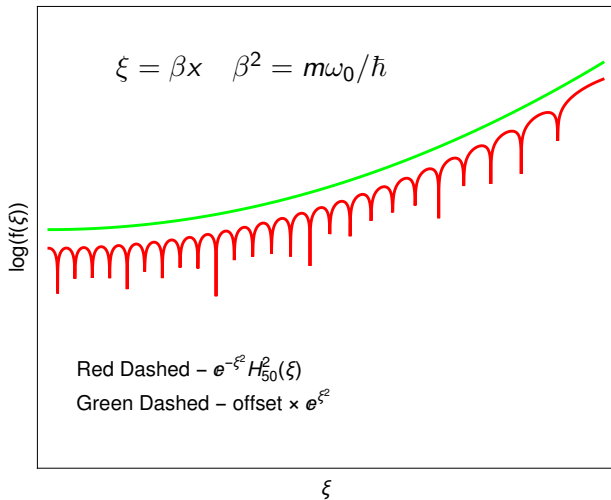
Notice.

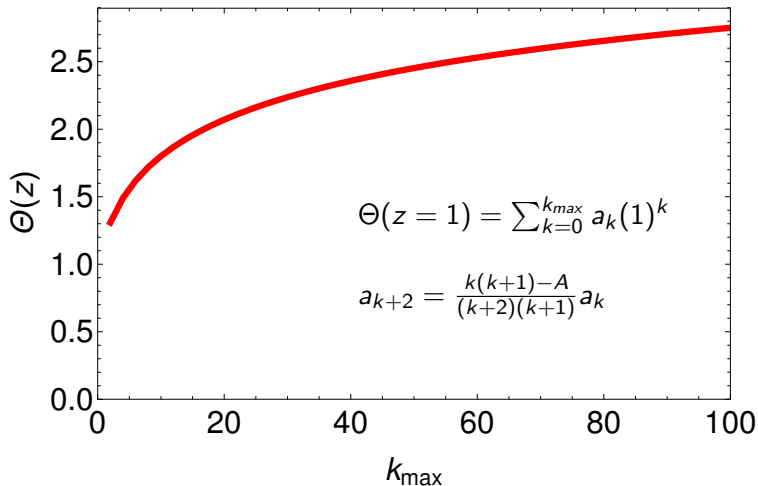
Given $a_0 \rightarrow a_2 \rightarrow a_4 \cdots$ and given $a_1 \rightarrow a_3 \rightarrow a_5 \cdots$

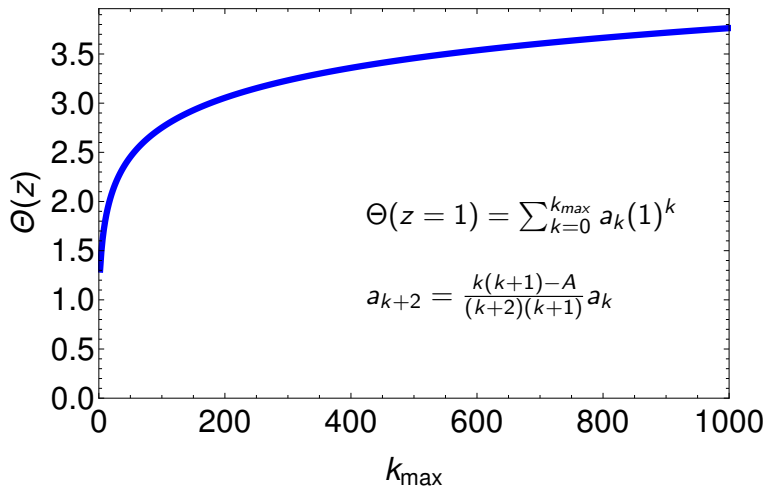
so

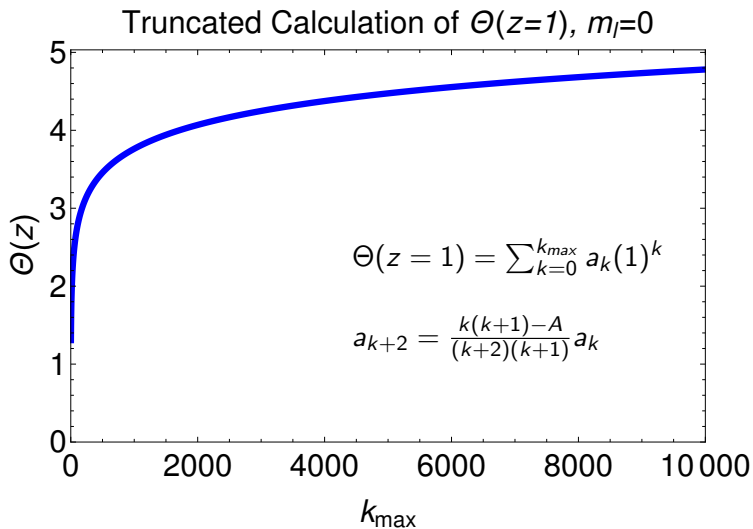
$$\Theta(z) = \sum_{k=0}^{\infty} a_k z^k = \sum_{\text{even}} a_k z^k + \sum_{\text{odd}} a_k z^k$$

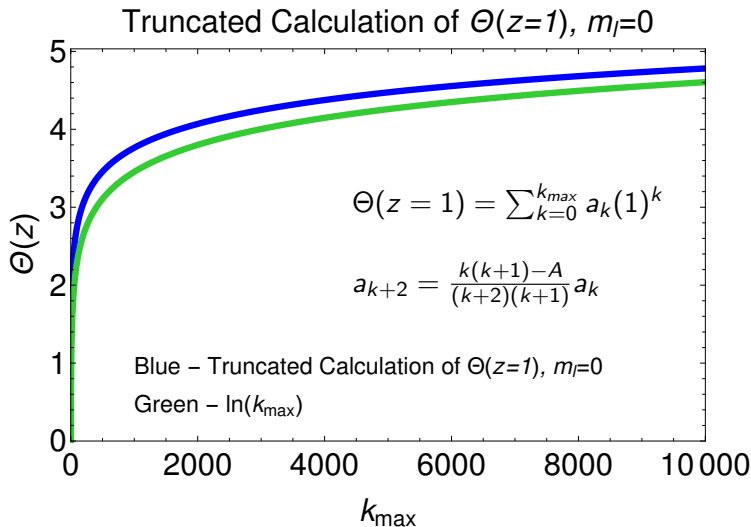
and we choose $a_0 = a_1 = 1$.



Truncated Calculation of $\Theta(z=1)$, $m_l=0$ 

Truncated Calculation of $\Theta(z=1)$, $m_l=0$ 





$$a_{k+2} = \frac{k(k+1) - A}{(k+2)(k+1)} a_k \quad m_\ell = 0 \quad a_0 = a_1 = 1$$

$$\Theta = P_\ell(z) = \sum_{\text{even/odd}}^{\ell} a_k z^k \quad z = \cos \theta$$

First few polynomials.

$$P_0(\cos \theta) = 1$$

$$P_3(\cos \theta) = \frac{1}{2} (5 \cos^3 \theta - 3 \cos \theta)$$

$$P_1(\cos \theta) = \cos \theta$$

$$P_4(\cos \theta) = \frac{1}{8} (35 \cos^4 \theta - 30 \cos^2 \theta + 3)$$

$$P_2(\cos \theta) = \frac{1}{2} (3 \cos^2 \theta - 1) \quad P_5(\cos \theta) = \frac{1}{8} (63 \cos^5 \theta - 70 \cos^3 \theta + 15 \cos \theta)$$

$$\Theta(\theta)\Phi(\phi) = Y_\ell^m(\theta, \phi) = \sqrt{\frac{2\ell + 1}{4\pi} \frac{(\ell - m)!}{(\ell + m)!}} P_\ell^m(\cos \theta) e^{im\phi}$$

$$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

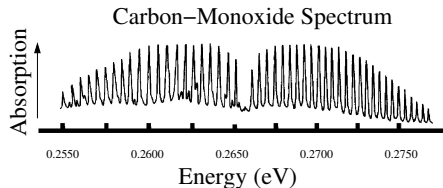
$$Y_1^1(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} \quad Y_1^{-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$$

$$Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$$

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$$E_\ell = \frac{\hbar^2}{2\mathcal{I}}\ell(\ell + 1)$$

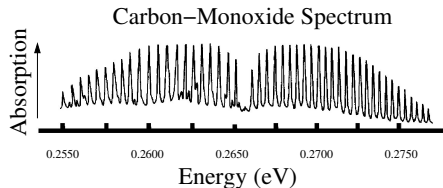
where \mathcal{I} is the moment of inertia. The vibrational part of the energy is described by the harmonic oscillator so $E_n = (n + \frac{1}{2})\hbar\omega_0$ with $\Delta E = \hbar\omega_0 = 0.25 \pm 0.05$ eV from our previous results. How do you get the expression above for the rotational energy? Is CO a rigid rotator?



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$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi + V(r)\psi = E\psi$$

$$\frac{p_r^2}{2\mu} = -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)$$

$$\frac{L^2}{2\mu r^2} = -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

$$m_\ell = 0, \pm \frac{1}{2}, \pm \frac{2}{2}, \pm \frac{3}{2}, \pm \frac{4}{2}, \pm \frac{5}{2}, \dots$$

$$\left[-\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{m_\ell^2}{\sin^2 \theta} \right] \Theta = A\Theta \quad A = \ell(\ell + 1)$$

$$L^2 |\phi_s\rangle = \hbar^2 \ell(\ell + 1) |\phi_s\rangle$$

$$\begin{aligned}\vec{L} &= \vec{r} \times \vec{p} \\ &= L_x \hat{i} + L_y \hat{j} + L_z \hat{k}\end{aligned}$$

$$\begin{aligned}\vec{L} &= \vec{r} \times \vec{p} \\ &= L_x \hat{i} + L_y \hat{j} + L_z \hat{k} \\ &= (yp_z - zp_y) \hat{i} + (zp_x - xp_z) \hat{j} + (xp_y - yp_x) \hat{k}\end{aligned}$$

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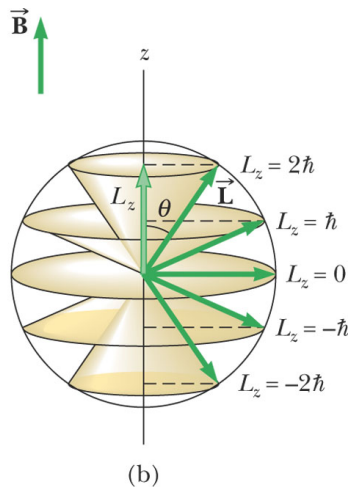
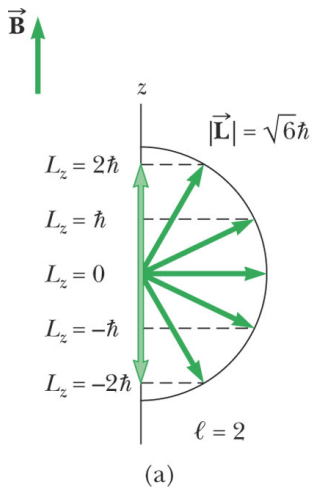
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Transformation from Cartesian to spherical coordinates:

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

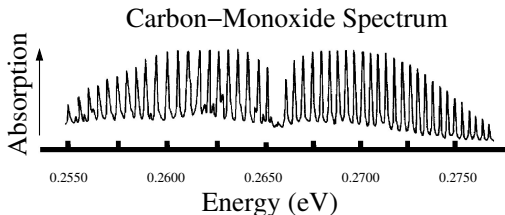


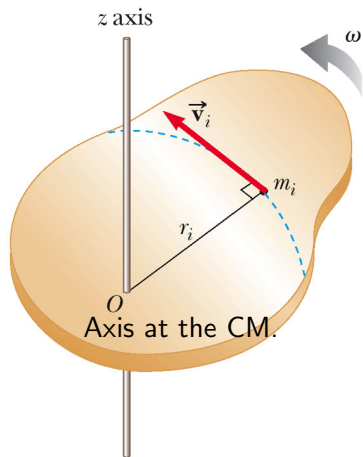
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Excited states of carbon monoxide (CO) can be observed by passing light through a cell containing CO and measuring the absorption spectrum shown below. The molecule can both vibrate and rotate at the same time. The rotational energy states of a rigid rotator are

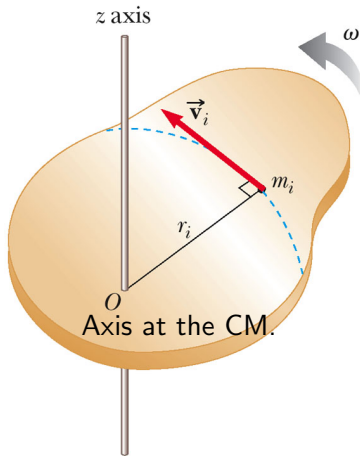
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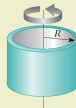
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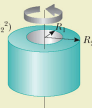
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TABLE 10.2 Moments of Inertia of Homogeneous Rigid Objects With Different Geometries

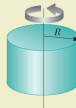
Hoop or thin cylindrical shell
 $I_{CM} = MR^2$



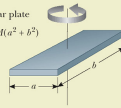
Hollow cylinder
 $I_{CM} = \frac{1}{2}M(R_1^2 + R_2^2)$



Solid cylinder or disk
 $I_{CM} = \frac{1}{2}MR^2$



Rectangular plate
 $I_{CM} = \frac{1}{12}M(a^2 + b^2)$



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Long thin rod with rotation axis through center
 $I_{CM} = \frac{1}{12}ML^2$



Long thin rod with rotation axis through end
 $I = \frac{1}{3}ML^2$



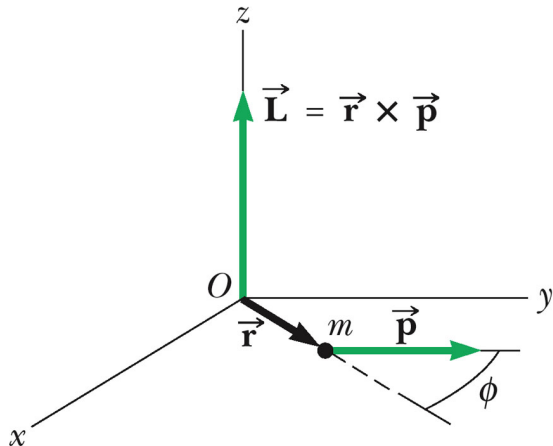
Solid sphere
 $I_{CM} = \frac{2}{5}MR^2$

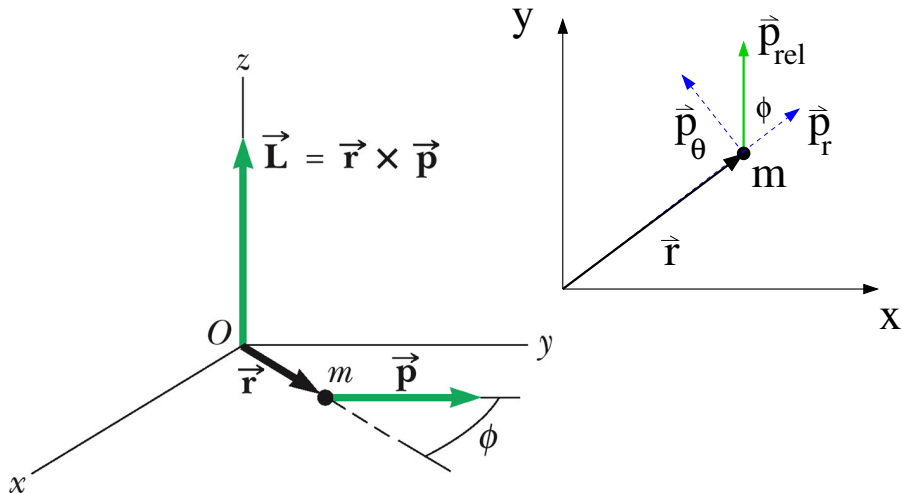


Thin spherical shell
 $I_{CM} = \frac{2}{3}MR^2$



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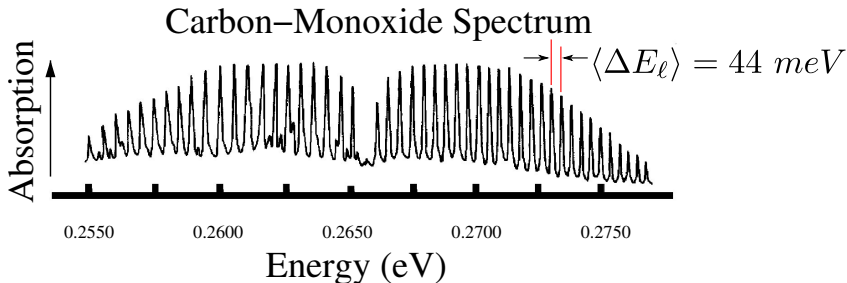
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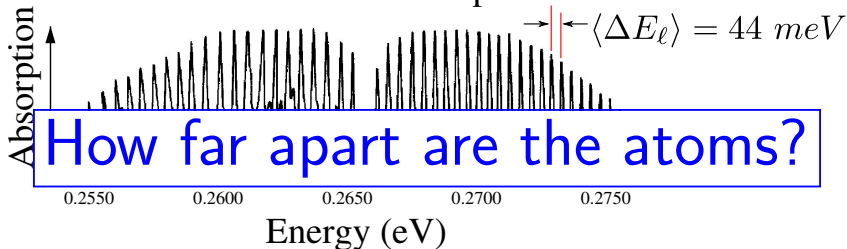


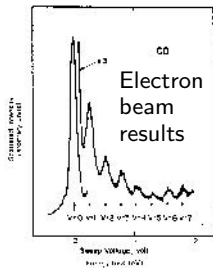
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Carbon–Monoxide Spectrum

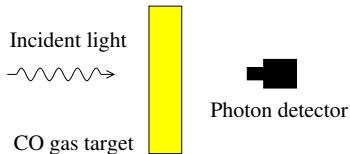




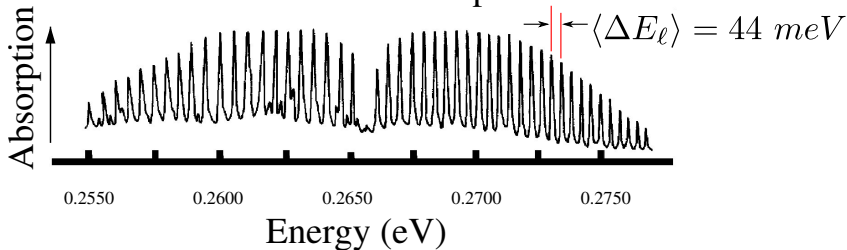
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$$\Delta E = 0.25 \pm 0.05 \text{ eV}$$

CO Absorption Spectrum



Carbon-Monoxide Spectrum



$$\begin{aligned}\vec{L} &= \vec{r} \times \vec{p} \\ &= L_x \hat{i} + L_y \hat{j} + L_z \hat{k}\end{aligned}$$

$$\begin{aligned}\vec{L} &= \vec{r} \times \vec{p} \\ &= L_x \hat{i} + L_y \hat{j} + L_z \hat{k} \\ &= (yp_z - zp_y) \hat{i} + (zp_x - xp_z) \hat{j} + (xp_y - yp_x) \hat{k}\end{aligned}$$

$$\begin{aligned}\vec{L} &= \vec{r} \times \vec{p} \\ &= L_x \hat{i} + L_y \hat{j} + L_z \hat{k} \\ &= (yp_z - zp_y) \hat{i} + (zp_x - xp_z) \hat{j} + (xp_y - yp_x) \hat{k} \\ &= \frac{\hbar}{i} \left[\left(y \frac{d}{dz} - z \frac{d}{dy} \right) \hat{i} + \left(z \frac{d}{dx} - x \frac{d}{dz} \right) \hat{j} + \left(x \frac{d}{dy} - y \frac{d}{dx} \right) \hat{k} \right]\end{aligned}$$

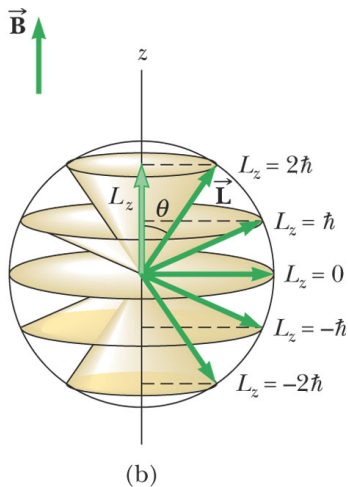
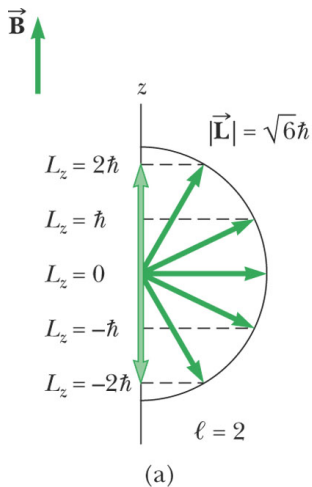
$$\begin{aligned}\vec{L} &= \vec{r} \times \vec{p} \\ &= L_x \hat{i} + L_y \hat{j} + L_z \hat{k} \\ &= (yp_z - zp_y) \hat{i} + (zp_x - xp_z) \hat{j} + (xp_y - yp_x) \hat{k} \\ &= \frac{\hbar}{i} \left[\left(y \frac{d}{dz} - z \frac{d}{dy} \right) \hat{i} + \left(z \frac{d}{dx} - x \frac{d}{dz} \right) \hat{j} + \left(x \frac{d}{dy} - y \frac{d}{dx} \right) \hat{k} \right]\end{aligned}$$

Transformation from Cartesian to spherical coordinates:

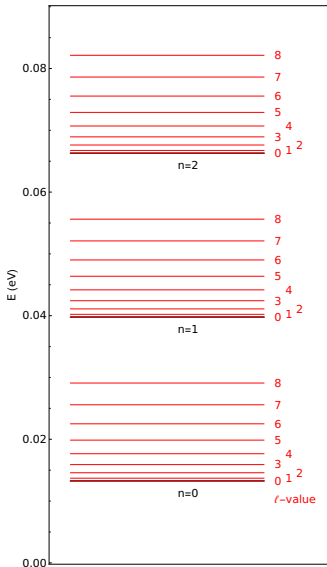
$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$



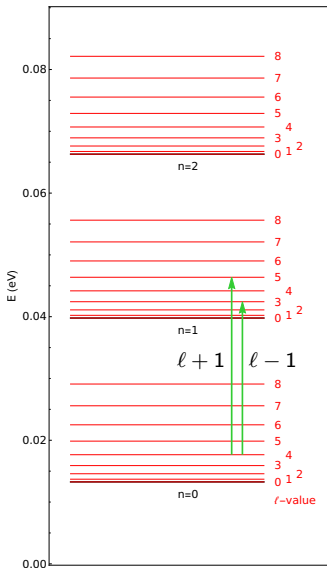
© 2006 Brooks/Cole - Thomson



$$E_{nl} = (n + \frac{1}{2})\hbar\omega_0 + \frac{\hbar^2}{2I}\ell(\ell + 1)$$

$$\Delta E_n = \hbar\omega_0 = 250 \pm 50 \text{ meV}$$

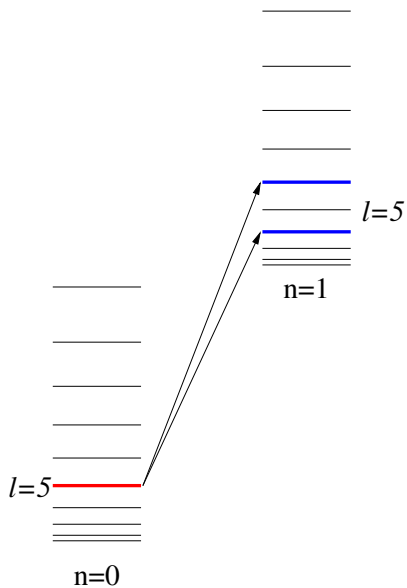
$$\Delta E_\ell = \frac{\hbar^2}{I} = 0.44 \pm 0.07 \text{ meV}$$



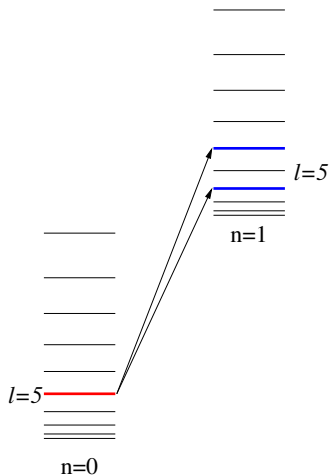
$$E_{n\ell} = (n + \frac{1}{2})\hbar\omega_0 + \frac{\hbar^2}{2I}\ell(\ell + 1)$$

$$\Delta E_n = \hbar\omega_0 = 250 \pm 50 \text{ meV}$$

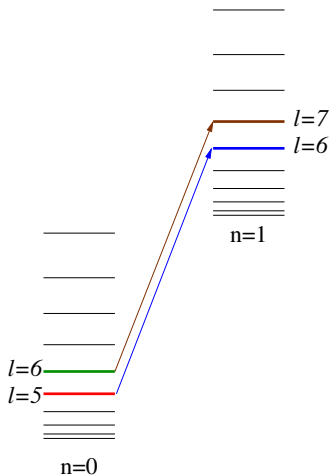
$$\Delta E_\ell = \frac{\hbar^2}{I} = 0.44 \pm 0.07 \text{ meV}$$



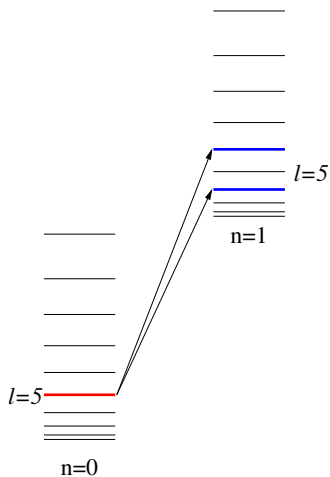
Vibration-Rotation

Adjacent Initial
Angular Momenta

$$l \rightarrow l+1$$



Vibration–Rotation

Adjacent Initial
Angular Momenta