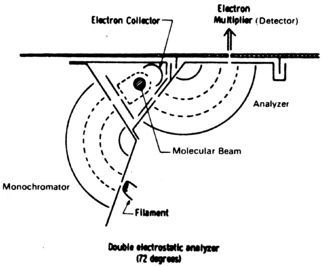
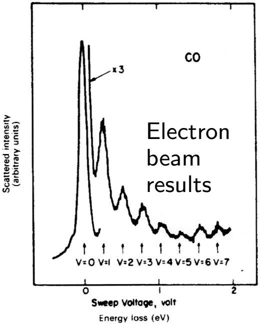
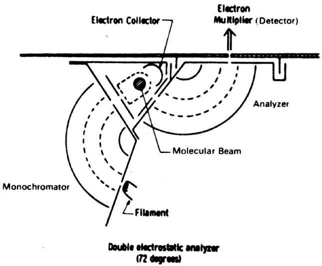


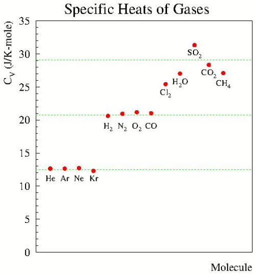
$\Delta E = 0.25 \pm 0.05 \ eV$



Electron beam results

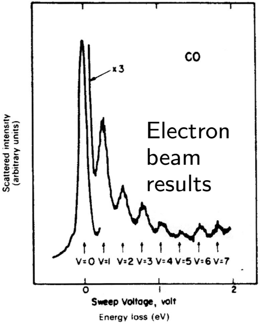
More On Carbon Monoxide 2



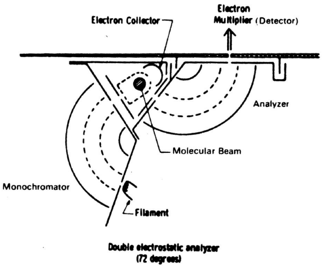


$\longrightarrow$

$\Delta E = 0.25 \pm 0.05 \ eV$



More On Carbon Monoxide



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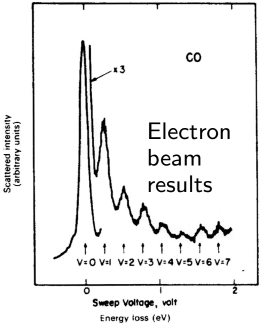
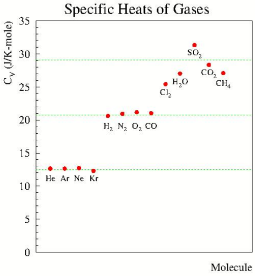
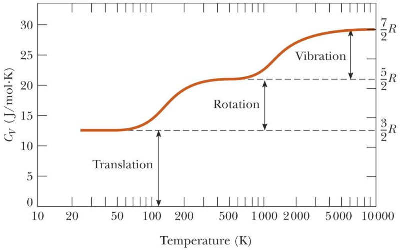
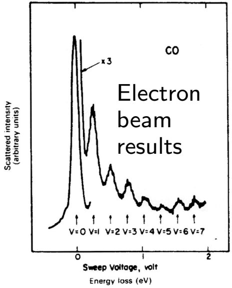






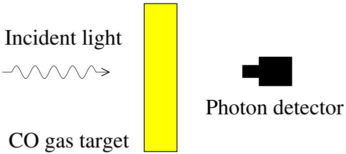
Even More On Carbon Monoxide



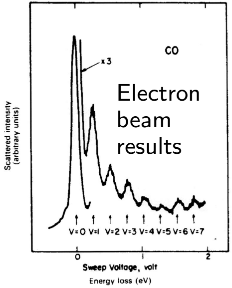
$\longrightarrow$

$\Delta E = 0.25 \pm 0.05 \ eV$

CO Absorption Spectrum



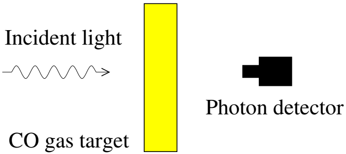
Even More On Carbon Monoxide



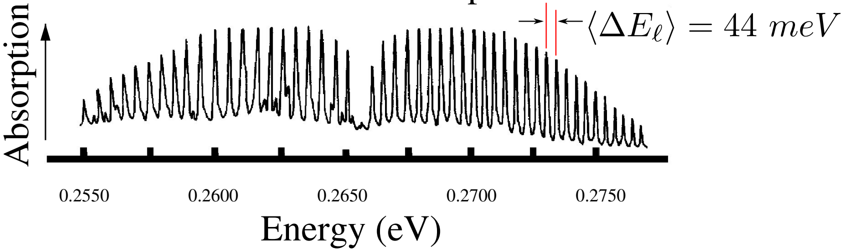
$\rightarrow$

$\Delta E = 0.25 \pm 0.05\ eV$

CO Absorption Spectrum



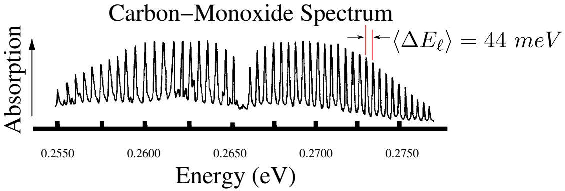
Carbon–Monoxide Spectrum



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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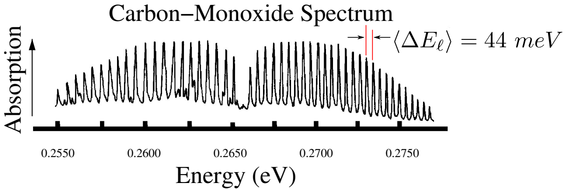
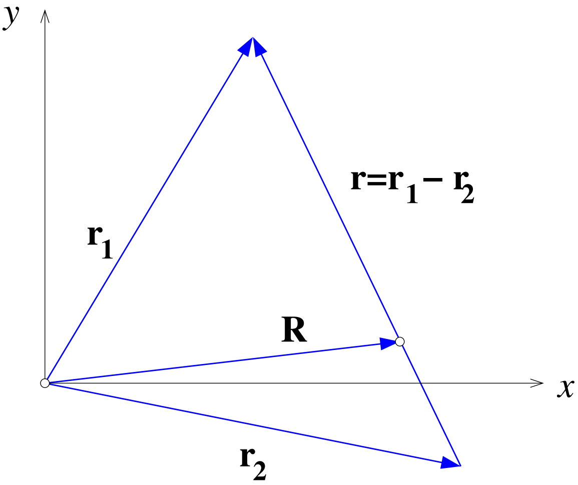
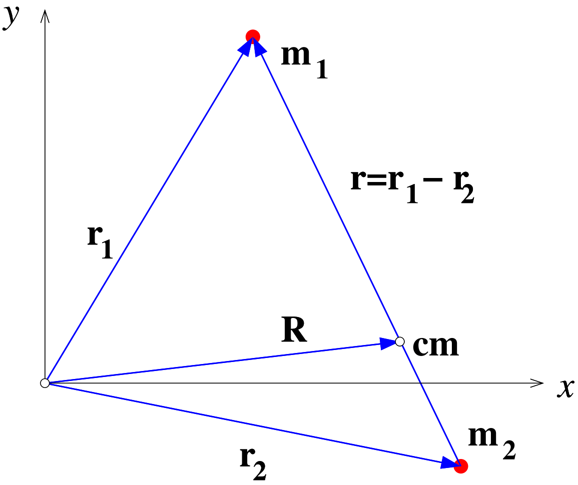
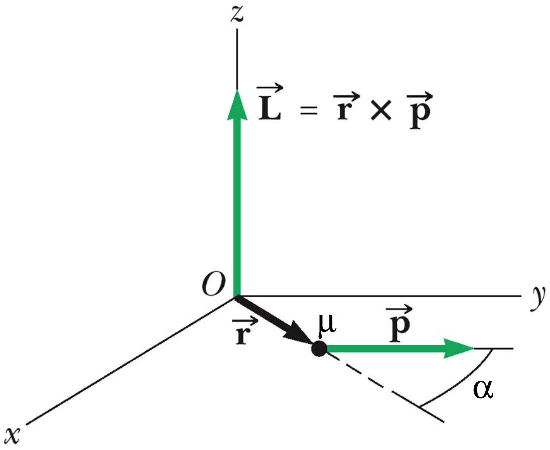
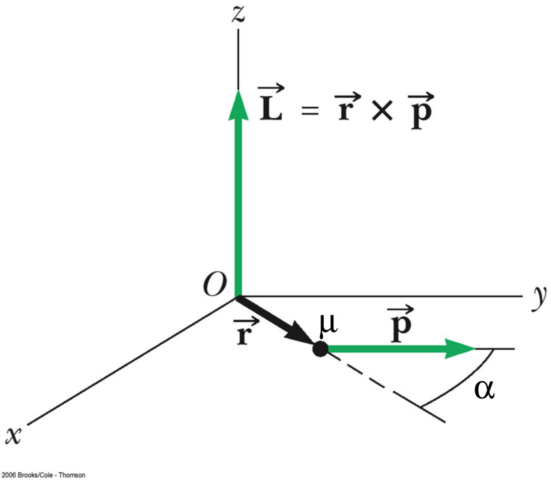


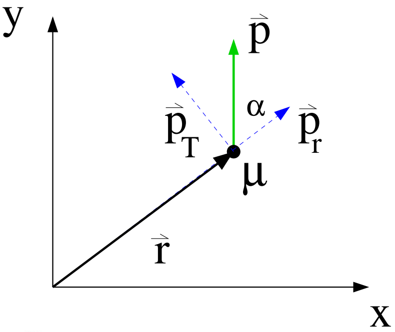
1. What is the kinetic and potential energy between the carbon and oxygen atoms in CO in the CM frame in cartesian and spherical coordinates?
2. How do you decompose the kinetic energy into radial and angular parts?
3. What is the Schroedinger equation for the rigid rotator?
4. What is the solution of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


y
r=r1 − r2
r1
R
x
r2


y
m 1
r=r 1 − r 2
r 1
R
cm
x
m 2
r 2


z
$\vec{L} = \vec{r} \times \vec{p}$
O
y
$\vec{r}$
μ
$\vec{p}$
α
x


z
$\vec{L} = \vec{r} \times \vec{p}$
O
y
$\vec{r}$
μ
$\vec{p}$
α
x
© 2006 Brooks/Cole - Thomson


y
$\vec{p}$
α
$\vec{p}_T$
$\vec{p}_r$
μ
$\vec{r}$
x

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

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

The Schroedinger Equation in 3D

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

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

Isolate ϕ-dependent part first.

$$-\left\{\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2\mu r^2\sin^2\theta}{\hbar^2}(E-V)\right\}=\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m_l^2$$

Isolate ϕ-dependent part first.

$$-\left\{\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2\mu r^2\sin^2\theta}{\hbar^2}(E-V)\right\}=\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m_l^2$$

Isolate θ-dependent part next.

$$-\left\{\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2\sin^2\theta}{\hbar^2}(E-V)\right\}=\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)-m_l^2$$

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

Isolate ϕ-dependent part first.

$$-\left\{\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2\mu r^2\sin^2\theta}{\hbar^2}(E-V)\right\}=\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m_l^2$$

Isolate θ-dependent part next.

$$-\left\{\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2\sin^2\theta}{\hbar^2}(E-V)\right\}=\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)-m_l^2$$

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

Change variable ($z=\cos\theta$).

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

Isolate ϕ-dependent part first.

$$-\left\{\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2\mu r^2\sin^2\theta}{\hbar^2}(E-V)\right\}=\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m_l^2$$

Isolate θ-dependent part next.

$$-\left\{\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2\sin^2\theta}{\hbar^2}(E-V)\right\}=\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)-m_l^2$$

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

Change variable ($z=\cos\theta$).

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

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 $m_\ell = 0$

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

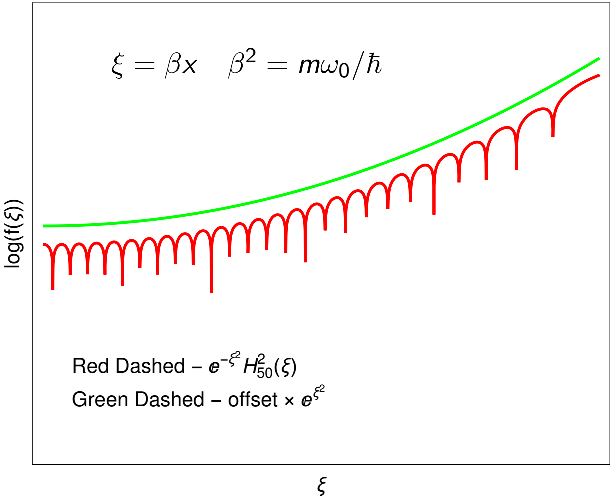
Notice.

$$\text{Given} \quad a_0 \to a_2 \to a_4 \cdots \quad \text{and given} \quad a_1 \to a_3 \to a_5 \cdots$$

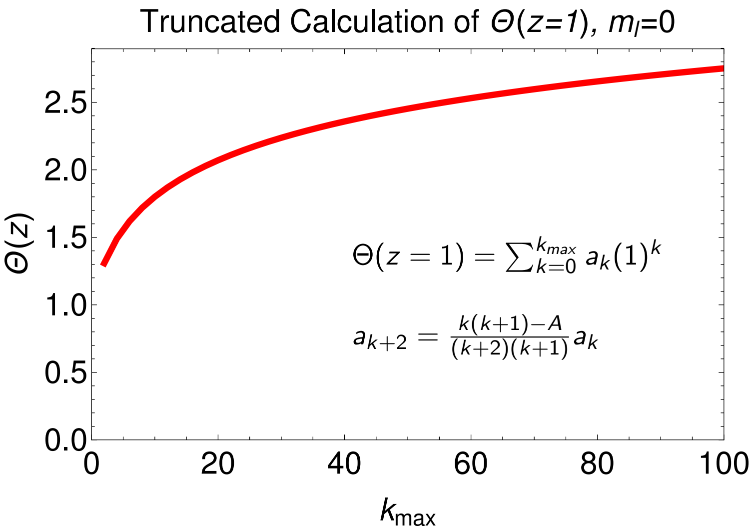
so

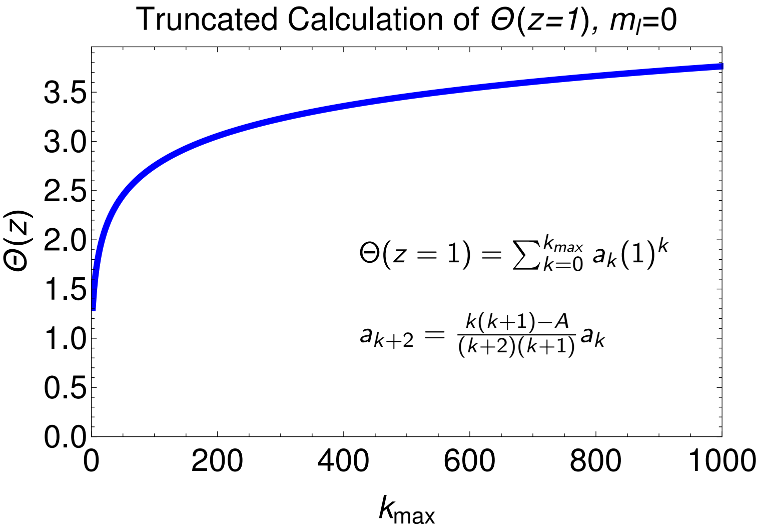
$$\Theta(z) = \sum_{k=0}^{\infty} a_k z^k = \sum_{even}^{\infty} a_k z^k + \sum_{odd}^{\infty} a_k z^k$$

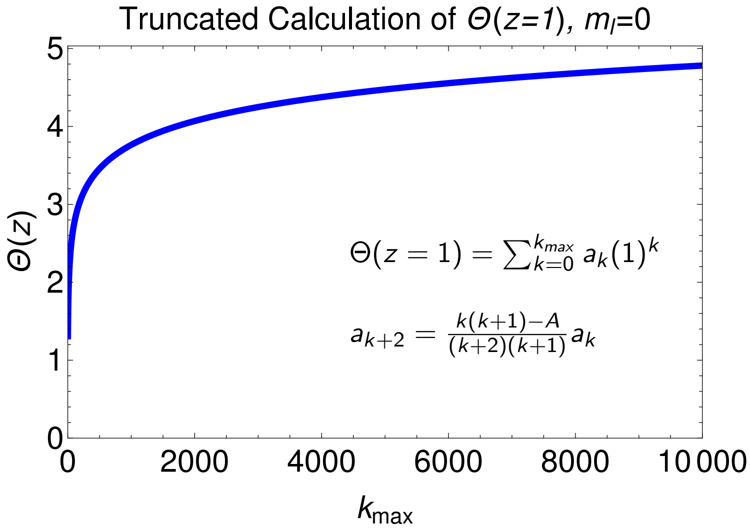
and we choose $a_0 = a_1 = 1$.

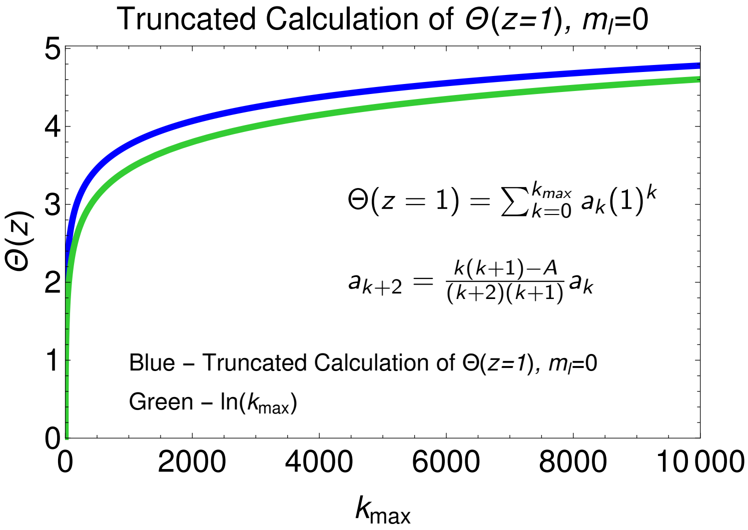

$\xi = \beta x \quad \beta^2 = m\omega_0/\hbar$
log(f(ξ))
Red Dashed – $e^{-\xi^2} H_{50}^2(\xi)$
Green Dashed – offset × e^{ξ^2}
ξ

Another Convergence Problem




Truncated Calculation of Θ(z=1), m_l=0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Θ(z)
0
200
400
600
800
1000
k_{max}
$\Theta(z = 1) = \sum_{k=0}^{k_{max}} a_k (1)^k$
$a_{k+2} = \frac{k(k+1)-A}{(k+2)(k+1)} a_k$


Truncated Calculation of Θ(z=1), m_l=0
5
4
3
2
1
0
Θ(z)
0
2000
4000
6000
8000
10 000
k_max
Θ(z = 1) = Σ_{k=0}^{k_max} a_k (1)^k
a_{k+2} = (k(k+1)−A)/((k+2)(k+1)) a_k


Truncated Calculation of Θ(z=1), m_l=0
5
4
3
2
1
0
Θ(z)
0
2000
4000
6000
8000
10 000
k_{max}
$\Theta(z=1) = \sum_{k=0}^{k_{max}} a_k (1)^k$
$a_{k+2} = \frac{k(k+1) - A}{(k+2)(k+1)} a_k$
Blue – Truncated Calculation of Θ(z=1), m_l=0
Green – ln(k_{max})

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

$$\Theta_{\ell 0} = P_\ell(z) = \sum_{even/odd}^{\ell} a_k z^k \qquad z = \cos\theta$$

First few polynomials.

$$P_0(\cos\theta) = 1 \qquad P_3(\cos\theta) = \frac{1}{2}\left(5\cos^3\theta - 3\cos\theta\right)$$

$$P_1(\cos\theta) = \cos\theta \qquad P_4(\cos\theta) = \frac{1}{8}\left(35\cos^4\theta - 30\cos^2\theta + 3\right)$$

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

Spherical Harmonics ($m_\ell = m$)

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

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

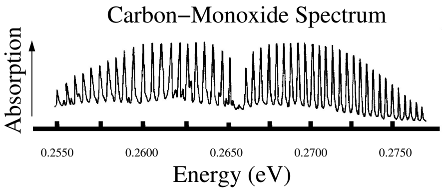
$$Y_1^1(\theta,\phi) = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} \qquad Y_1^{-1}(\theta,\phi) = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$$

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

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? Explain the spectrum below.



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

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

$$m_\ell = 0, \pm1, \pm2, \pm3, \pm4, \pm5, \ldots$$

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

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

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

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

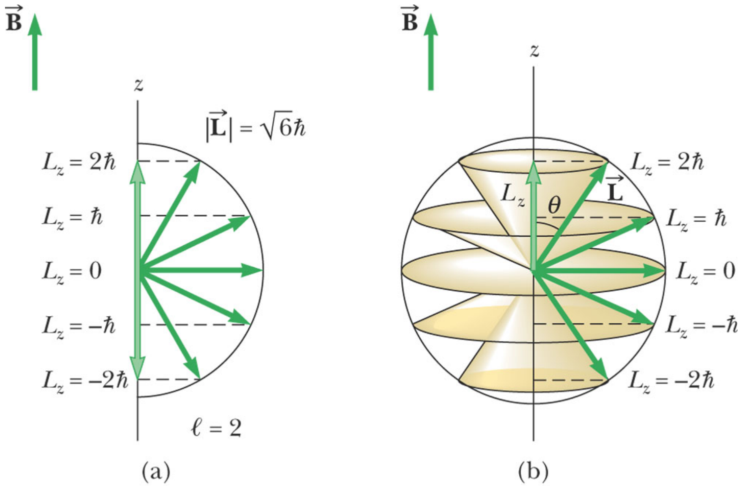
$$\begin{aligned}
\vec{L} &= \vec{r} \times \vec{p} \\
&= L_x \hat{i} + L_y \hat{j} + L_z \hat{k} \\
&= (yp_z - zp_y)\,\hat{i} + (zp_x - xp_z)\,\hat{j}\, + (xp_y - yp_x)\,\hat{k} \\
&= \frac{\hbar}{i}\left[\left(y\frac{d}{dz} - z\frac{d}{dy}\right)\hat{i} + \left(z\frac{d}{dx} - x\frac{d}{dz}\right)\hat{j}\,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

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

Transformation from Cartesian to spherical coordinates:

$$
\begin{aligned}
x &= r\sin\theta\cos\phi \\
y &= r\sin\theta\sin\phi \\
z &= r\cos\theta
\end{aligned}
$$

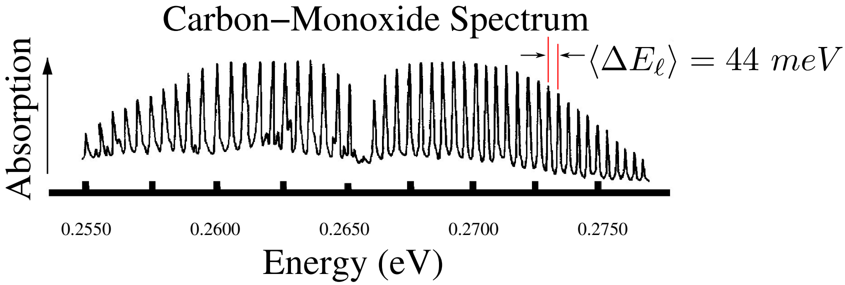
The Eigenvalues of $\hat{L}^2$ and L_z

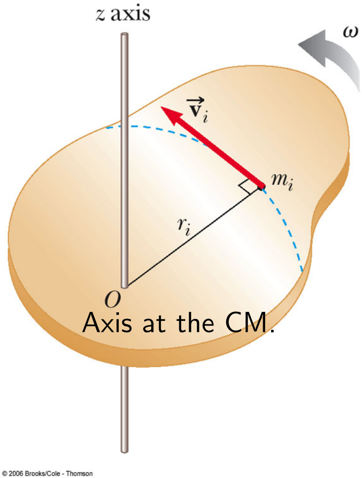


Excited states of carbon monoxide (CO) can be observed by passing light through a cell containing CO and measuring the absorption spectrum shown below. The molecule can vibrate and rotate at the same time. The rotational energy states of a rigid rotator are

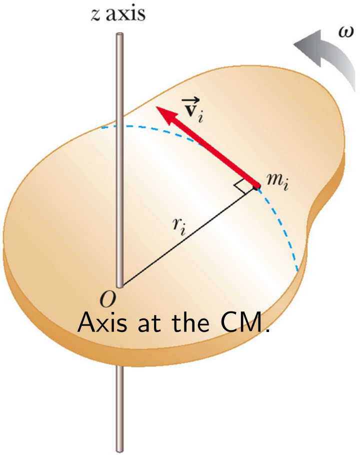
$$E_\ell = \frac{\hbar^2}{2\mathcal{I}}\ell(\ell+1)$$

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 does one obtain the expression above for the rotational energy? Is CO a rigid rotator?

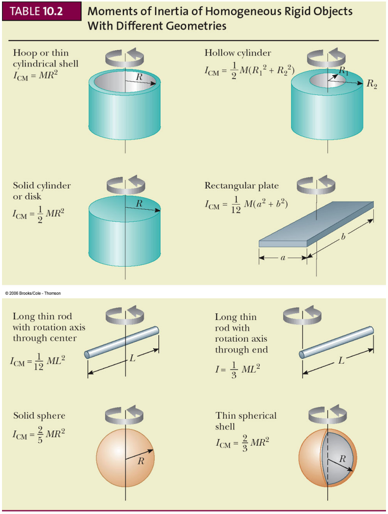




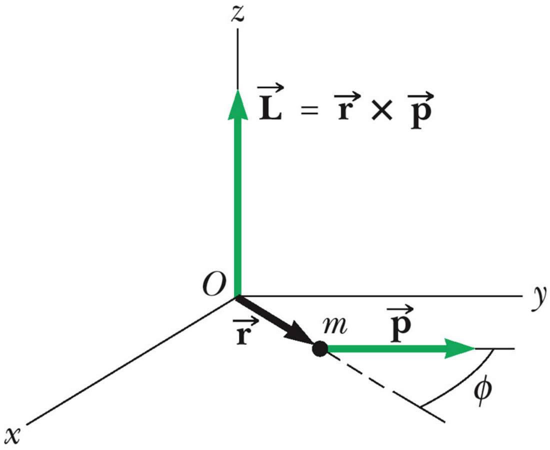
Axis at the CM.



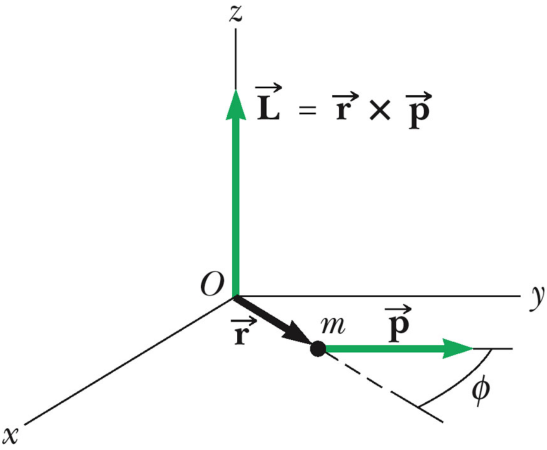
Axis at the CM.

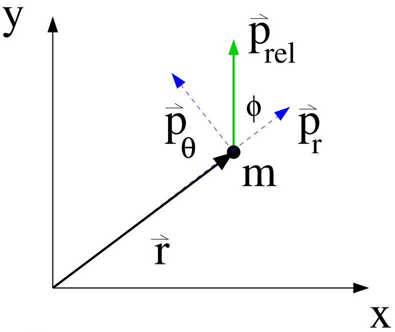


Angular Momentum



Angular Momentum

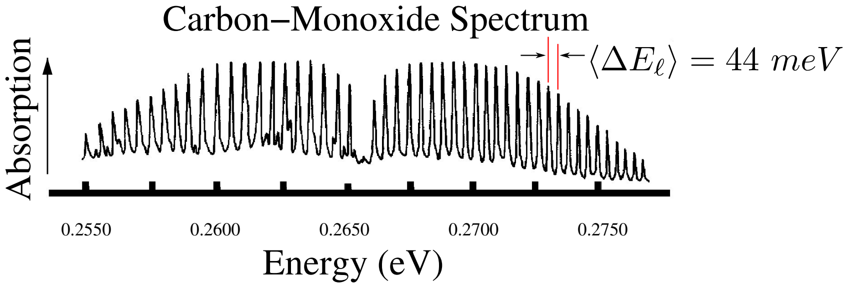


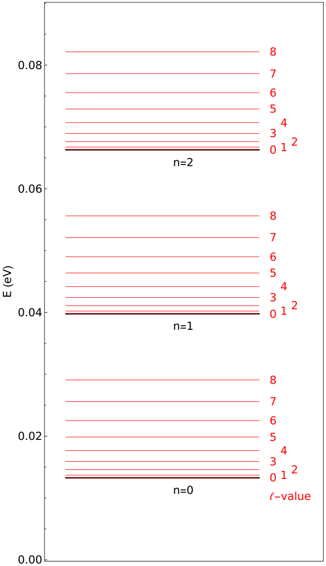


Excited states of carbon monoxide (CO) can be observed by passing light through a cell containing CO and measuring the absorption spectrum shown below. The molecule can vibrate and rotate at the same time. The rotational energy states of a rigid rotator are

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

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 does one obtain the expression above for the rotational energy? Is CO a rigid rotator?

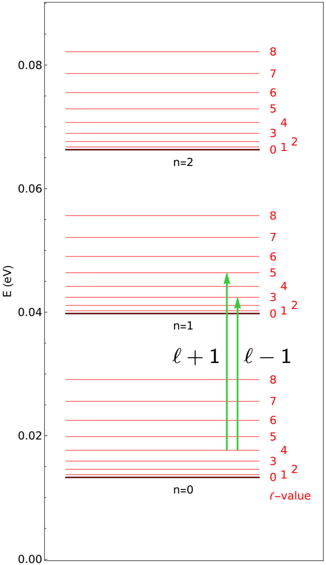




$$E_{nl} = (n + \frac{1}{2})\hbar\omega_0 + \frac{\hbar^2}{2\mathcal{I}}\ell(\ell+1)$$

$$\Delta E_n = \hbar\omega_0 = 250 \pm 50 \;\; meV$$

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



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

$$\Delta E_n = \hbar\omega_0 = 250 \pm 50 \;\; meV$$

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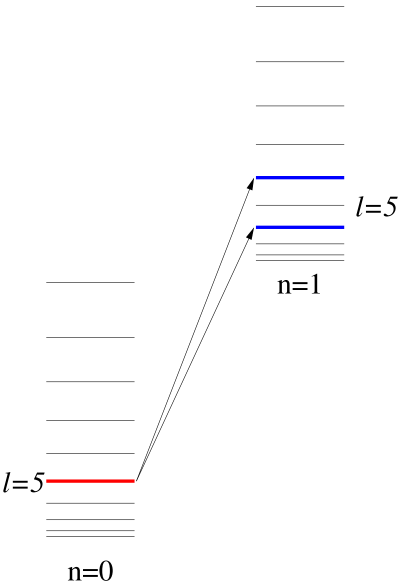
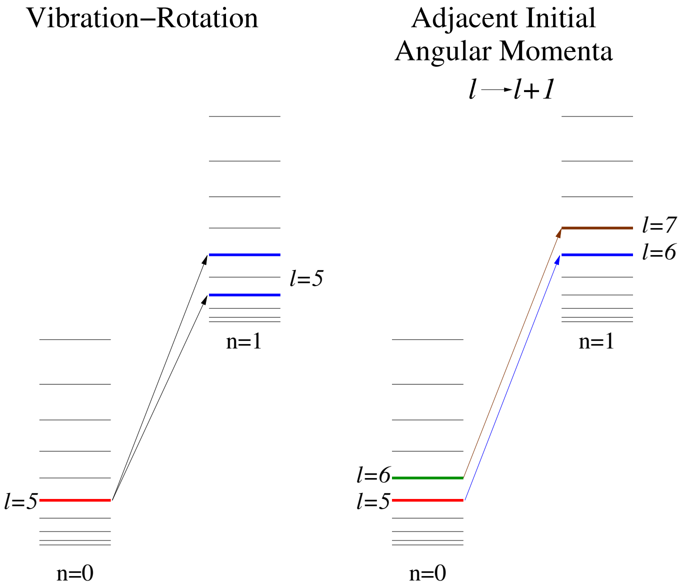
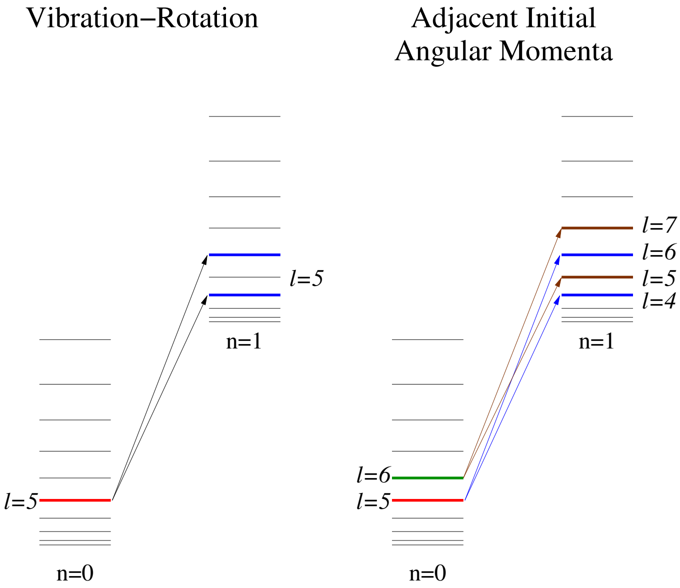
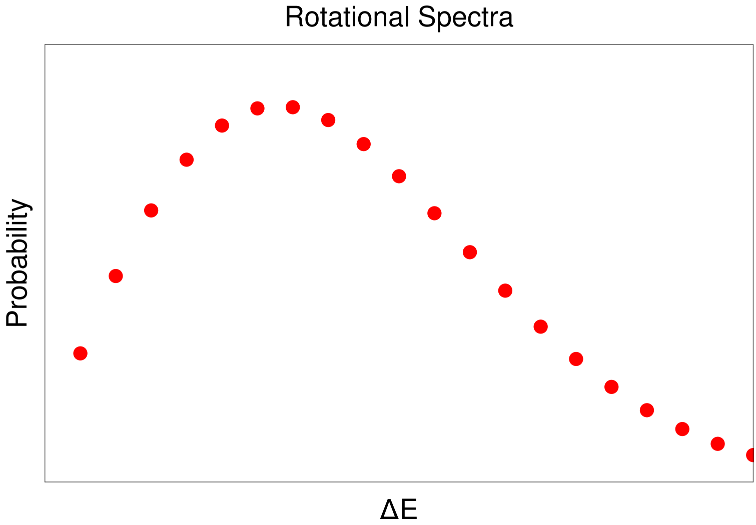


l=5
n=1
l=5
n=0


Vibration–Rotation
l=5
l=5
n=1
n=0
Adjacent Initial
Angular Momenta
l → l+1
l=7
l=6
n=1
l=6
l=5
n=0



Vibration−Rotation
l=5
l=5
n=1
n=0
Adjacent Initial
Angular Momenta
l=7
l=6
l=5
l=4
n=1
l=6
l=5
n=0


Rotational Spectra
Probability
ΔE