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Department of Chemistry

Physical Chemistry 2

Lecture 8. The Rigid Rotor (2)

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PChem 2

Physical Chemistry 2

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Topics in Lecture 8

Rigid rotor model

Spherical harmonics

IR spectroscopy

In Atkins' *Physical Chemistry* (11th ed.),

7F Rotational motion

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Rigid Rotator

Full Hamiltonian is

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

Therefore, we can derive $\hat{L}^2$ operator from the relation

$$\hat{H} = \frac{\hat{L}^2}{2I}, \quad \hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

The equation is fully *angular*. It depends to only angular variables.

$$\hat{H}Y(\theta,\phi) = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right]$$

The eigenfunction of this equation is very well-known special function, called *spherical harmonics*.

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Spherical harmonics

Assume that

$$\hat{H}Y(\theta,\phi) = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right] = -\frac{\hbar^2 l(l+1)}{2I}Y(\theta,\phi)$$

Therefore

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right] = -\,l(l+1)$$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -\,l(l+1)Y\sin^2\theta$$

Separation of variables: $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

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Spherical harmonics

Plug in and divide by $\Theta\Phi$.

$$\left\{ \frac{1}{\Theta} \left[\sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1)\sin^2\theta \right\} + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = 0$$

Set separation constant

$$\frac{1}{\Theta} \left[\sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1)\sin^2\theta = m^2, \qquad \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = -m^2$$

The ϕ equation is easy: we have solved this already.

$$\Phi(\phi) = e^{im\phi}, \quad (m \in \mathbb{Z})$$

The θ equation is:

$$\sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + (l(l+1)\sin^2\theta - m^2)\Theta = 0$$

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The solution of this equation is

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + (l(l+1)\sin^2\theta - m^2)\Theta = 0 \quad \Longrightarrow \quad \Theta(\theta) = AP_l^m(\cos\theta)$$

where P_l^m is the *associated Legendre function*.

$$P_l^m(x) = (-1)^m(1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_l(x)$$

$$P_l(x) = \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2-1)^l$$

They are defined from the *Legendre polynomial* P_l, where Legendre polynomials are defined by *Rodrigues formula*.

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Spherical harmonics

The Legendre polynomials are well-known special functions.

Table 4.1: *The first few Legendre polynomials, $P_\ell(x)$: (a) functional form, (b) graph.*

$$P_0 = 1$$

$$P_1 = x$$

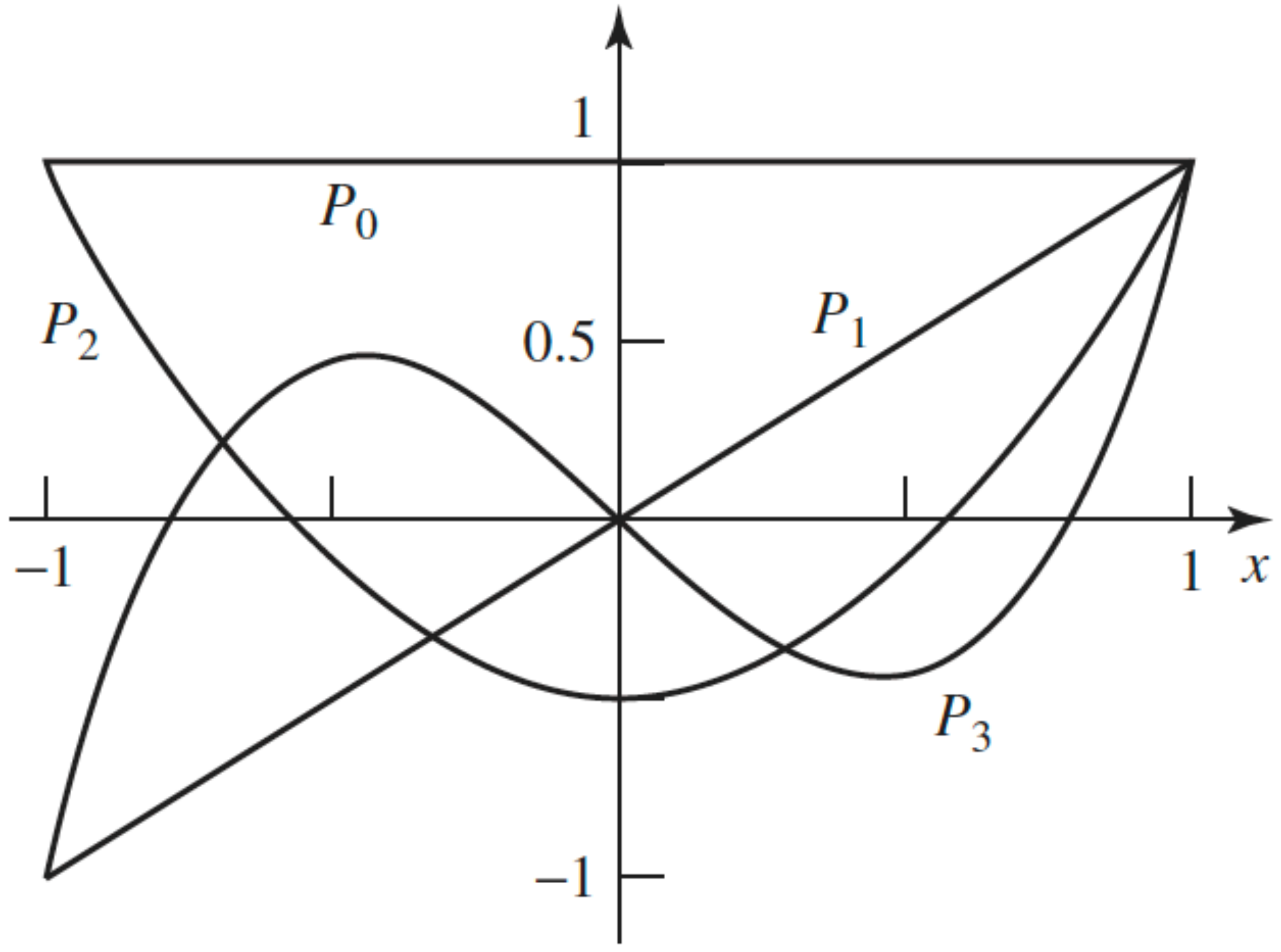
$$P_2 = \frac{1}{2}(3x^2 - 1)$$

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

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

$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$

(a)



(b)

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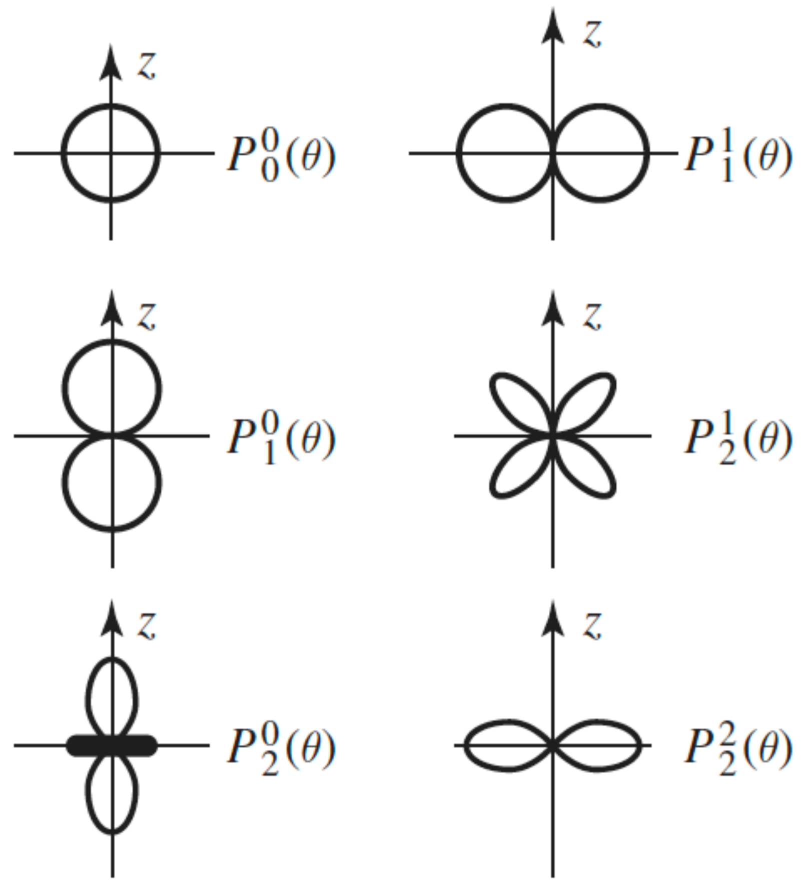
Table 4.2: *Some associated Legendre functions,* $P_\ell^m(\cos\theta)$*: (a) functional form, (b) graphs of* $r = |P_\ell^m(\cos\theta)|$ *(in these plots r tells you the magnitude of the function in the direction* θ*; each figure should be rotated about the z axis).*

$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$
$P_1^1 = -\sin\theta$	$P_3^3 = -15\sin\theta(1-\cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = -\frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = -3\sin\theta\cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$

(a)



(b)

Table 4.3: *The first few spherical harmonics,* $Y_\ell^m(\theta,\phi)$.

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm2} = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{\pm2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm1} = \mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi}$	$Y_3^{\pm1} = \mp\left(\frac{21}{64\pi}\right)^{1/2}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$	$Y_3^{\pm2} = \left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta e^{\pm2i\phi}$
$Y_2^{\pm1} = \mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm3} = \mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta e^{\pm3i\phi}$

By multiplying associated Legendre function and $\Phi(\phi)$, we yield spherical harmonics.

$$Y_l^m(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}e^{im\phi}P_l^m(\cos\theta)$$

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Rigid rotor

The energy level of rigid rotor is

$$\hat{H}Y(\theta,\phi) = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right] = -\frac{\hbar^2 l(l+1)}{2I}Y(\theta,\phi)$$

Therefore,

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

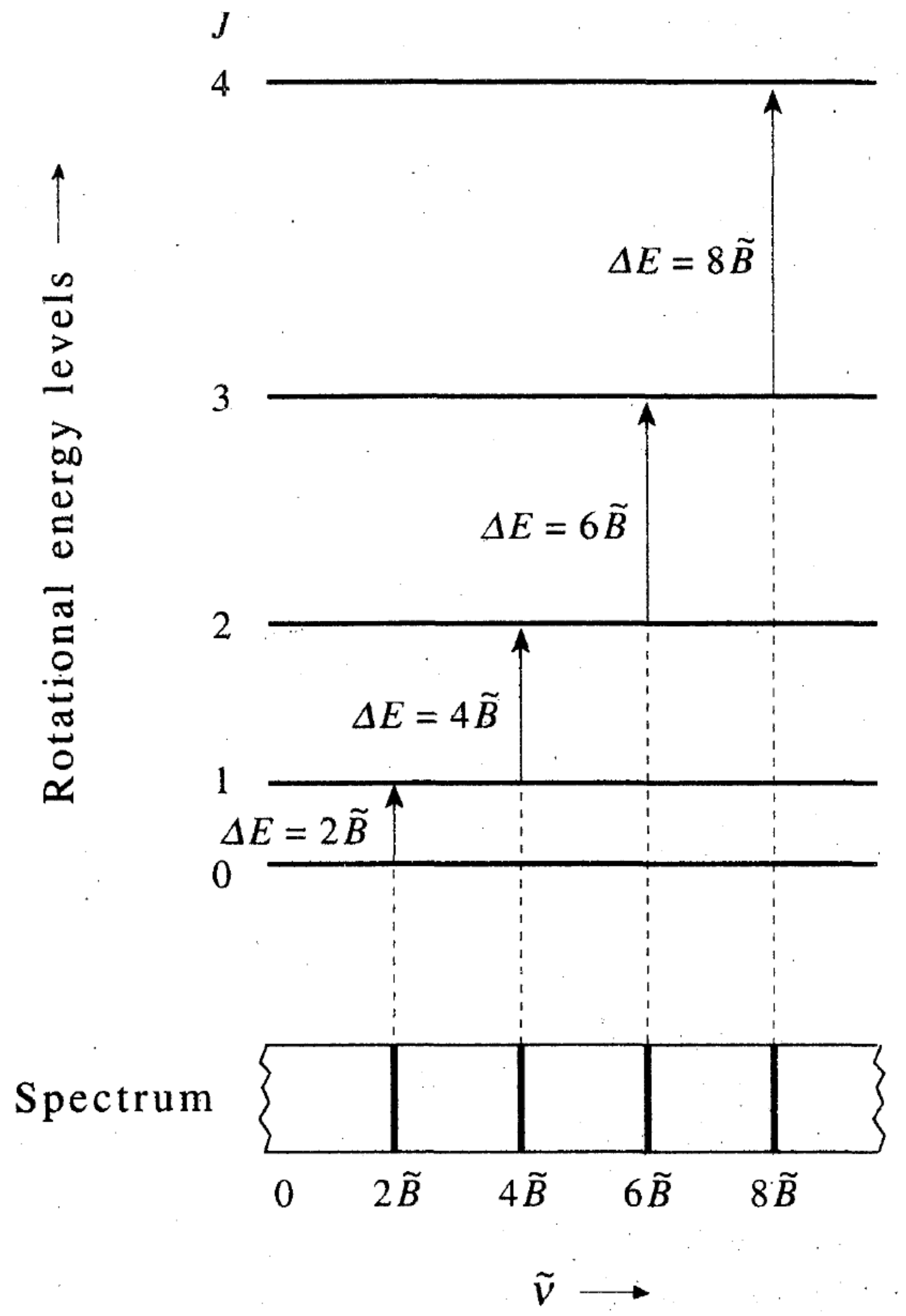
Selection rules are

$$\Delta J = \pm 1$$

$$\Delta E = E_{J+1} - E_J = \frac{h^2}{4\pi^2 I}(J+1)$$

$$\nu = \frac{h}{4\pi^2 I}(J+1) = 2B(J+1),\ B = \frac{h}{8\pi^2 I}$$

$$\tilde{\nu} = 2\tilde{B}(J+1), \quad \tilde{B} = \frac{h}{8\pi^2 cI}$$



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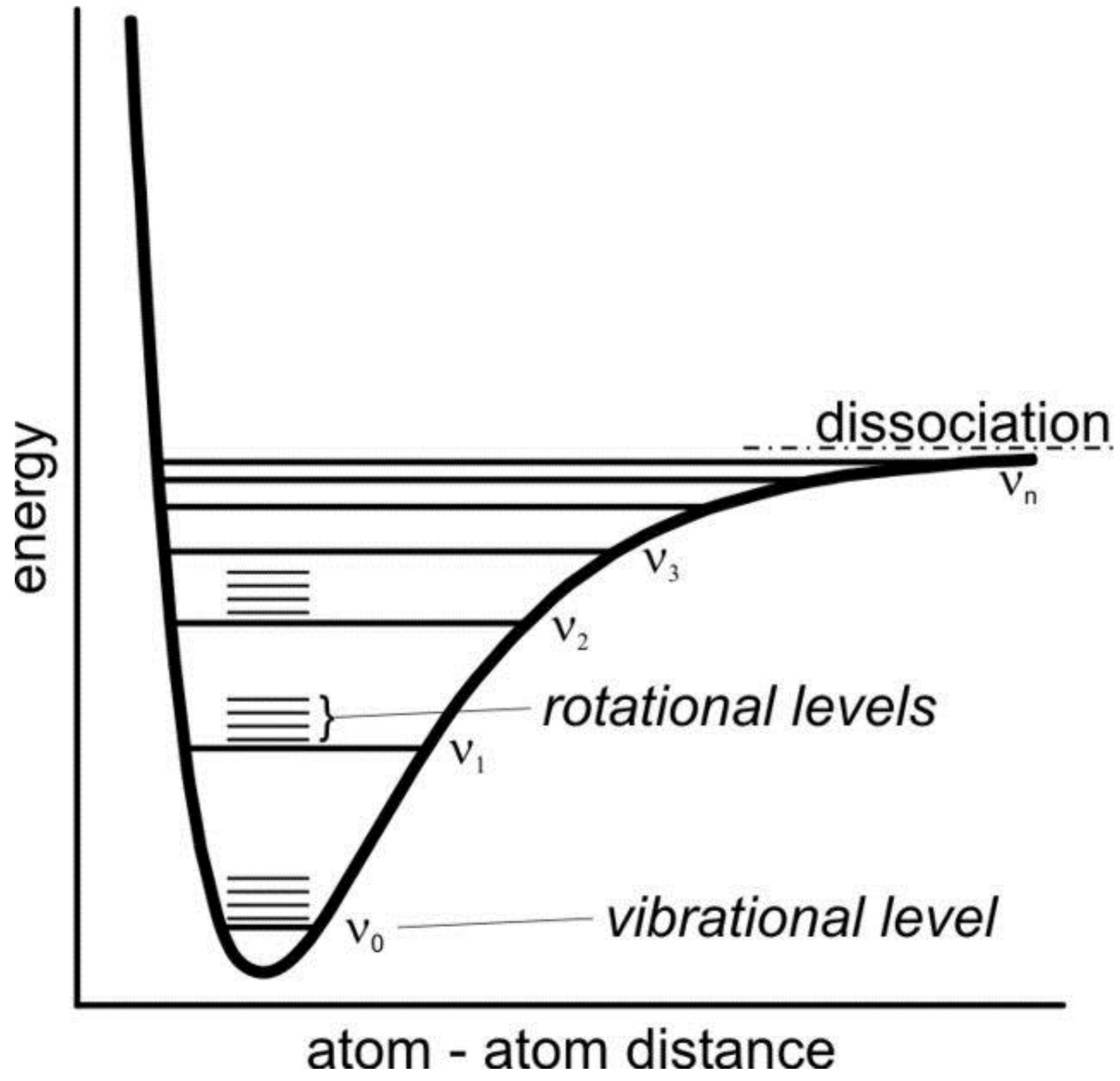
Vibrational-rotational energy level



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