

Tema 7.-Espectroscopía vibracional y rotacional

7.1. Interacción de la radiación con la materia

7.2. Absorción, emisión espontánea y emisión estimulada

7.3. Reglas de selección

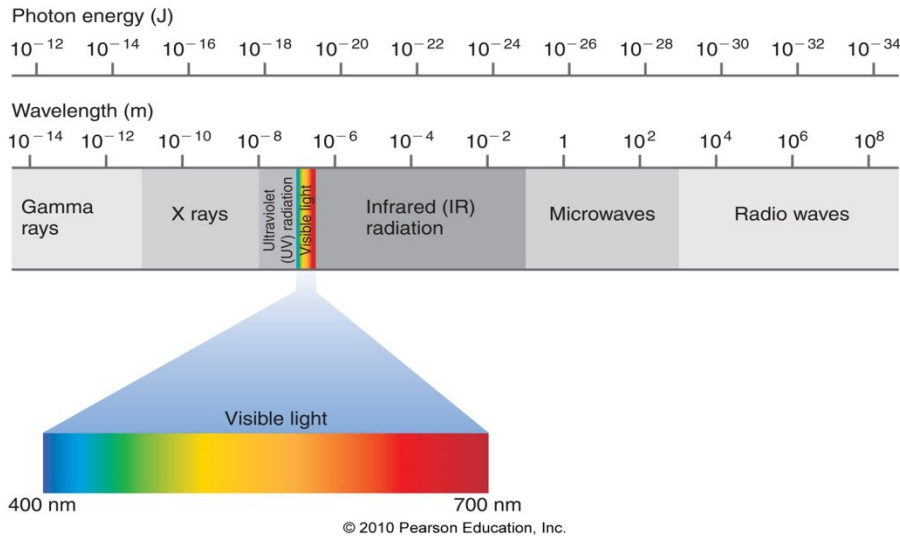
7.4. Espectroscopía vibracional

7.5. Espectroscopía rotacional

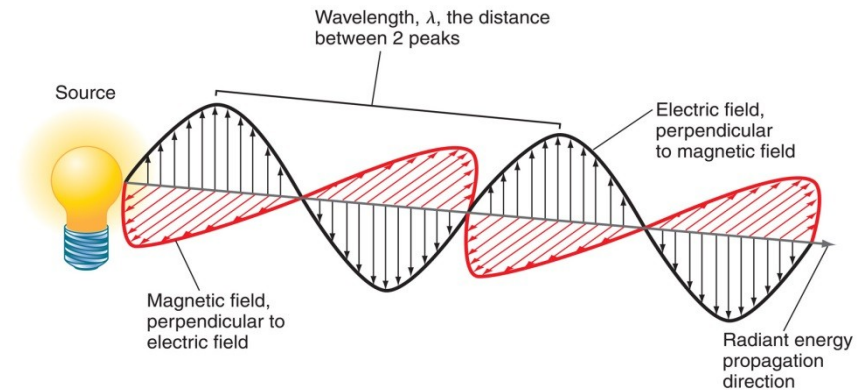
7.6 Efecto Raman

Interacción de la radiación con la materia

El espectro electromagnético



Campo electromagnético asociado a una onda de luz



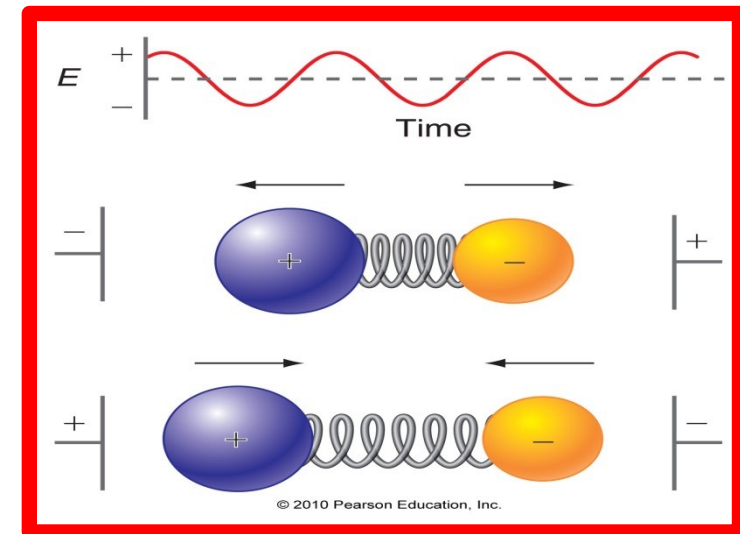
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TABLE 19.1 IMPORTANT SPECTROSCOPIES AND THEIR SPECTRAL RANGE

Spectral Range	λ (m)	ν (Hz)	$\tilde{\nu}$ (cm^{-1})	Energy (J)	Spectroscopy
Radio	>0.1	$<3 \times 10^9$	>0.1	$<2 \times 10^{-24}$	NMR
Microwave	$0.001 - 0.1$	$3 \times 10^9 - 3 \times 10^{11}$	$0.1 - 10$	$2 \times 10^{-24} - 2 \times 10^{-22}$	Rotational
Infrared	$7 \times 10^{-7} - 1 \times 10^{-3}$	$3 \times 10^{11} - 4 \times 10^{14}$	$10 - 1 \times 10^4$	$2 \times 10^{-22} - 3 \times 10^{-19}$	Vibrational
Visible	$4 \times 10^{-7} - 7 \times 10^{-7}$	$4 \times 10^{14} - 7 \times 10^{14}$	$1 \times 10^4 - 3 \times 10^4$	$3 \times 10^{-19} - 5 \times 10^{-19}$	Electronic
Ultraviolet	$1 \times 10^{-8} - 4 \times 10^{-7}$	$7 \times 10^{14} - 3 \times 10^{16}$	$3 \times 10^4 - 1 \times 10^6$	$5 \times 10^{-19} - 2 \times 10^{-17}$	Electronic

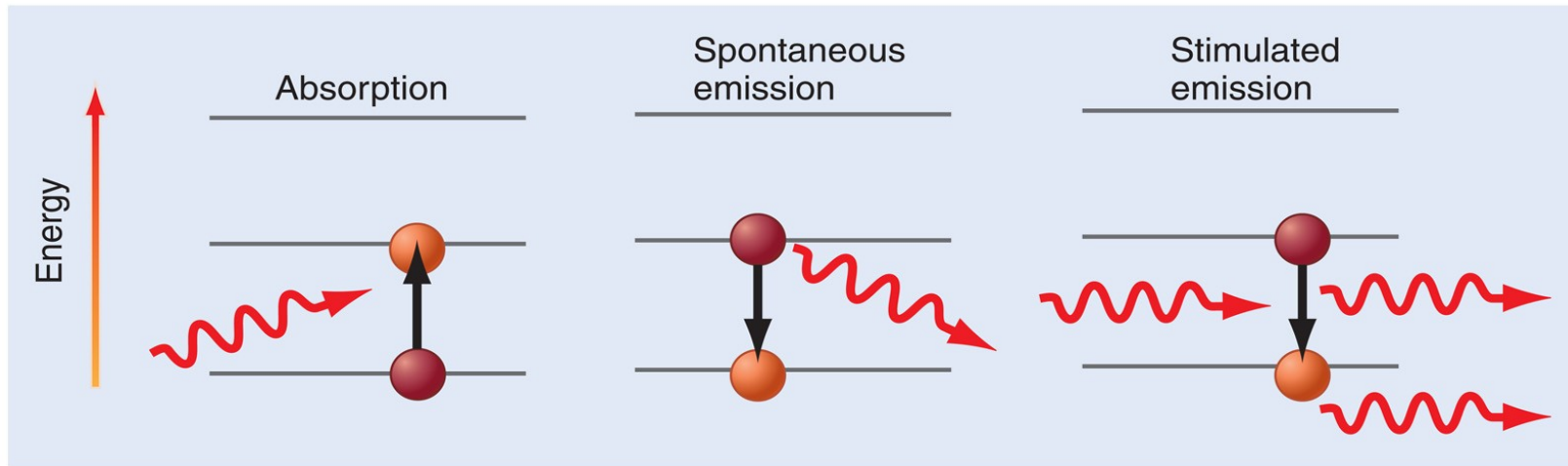
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$$E = h\nu = hc \left\{ \frac{hc}{\lambda} \right\} \nu$$

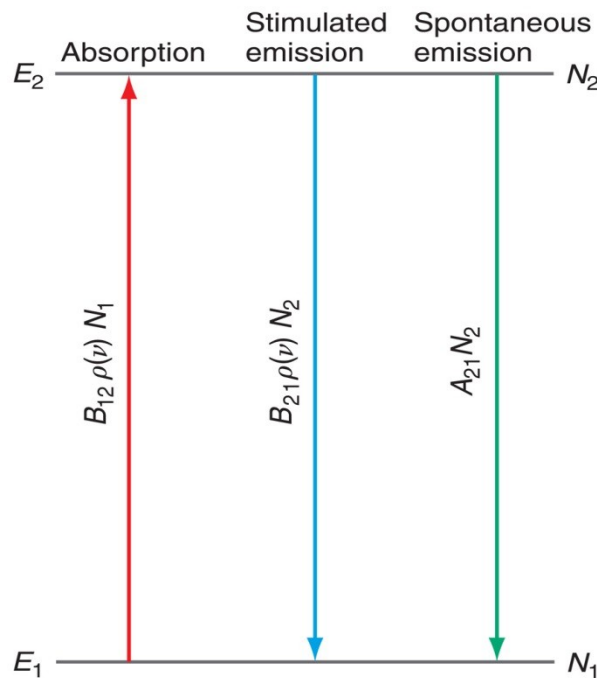


La interacción de un dipolo eléctrico oscilante con un campo eléctrico variable es la base de la interacción radiación-materia

Absorción y Emisión



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En el equilibrio (condiciones fotoestacionarias)

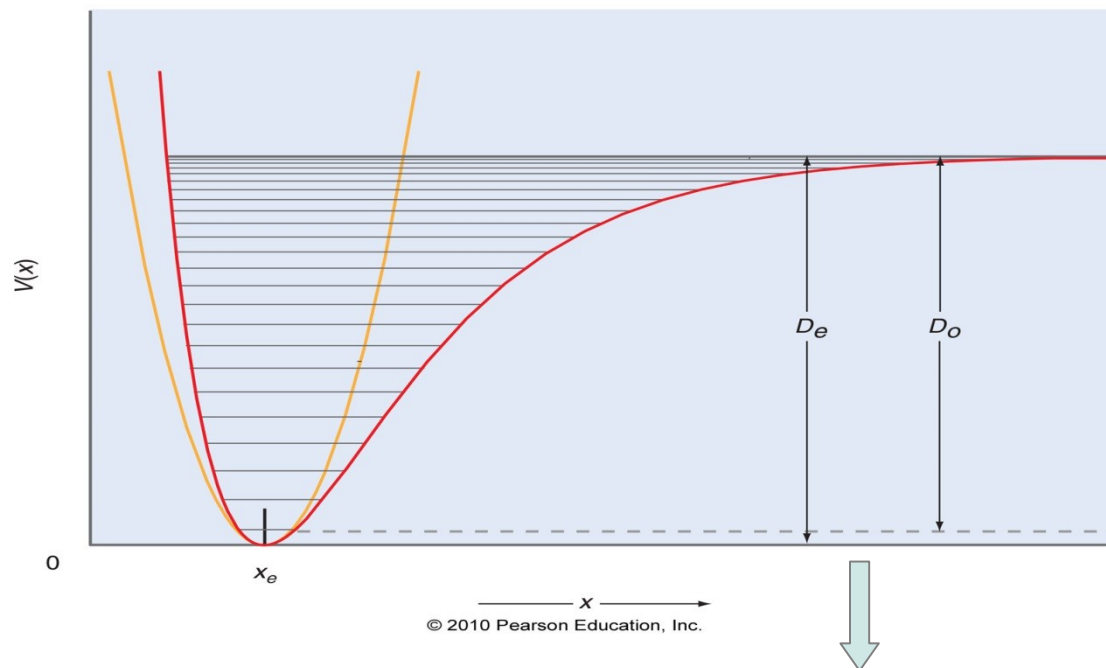
nº procesos absorción = nº procesos emisión

$$B_{12}\rho(\nu)N_1 = B_{21}\rho(\nu)N_2 + A_{21}N_2$$

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$$B_{12} = B_{21} \quad \text{and} \quad \frac{A_{21}}{B_{21}} = \frac{16\pi^2\hbar\nu^3}{c^3}$$

Coeficientes de Einstein



Potencial anarmónico de Morse

$$V(x) = D_e \left[1 - e^{-\alpha(x-x_e)} \right]^2$$

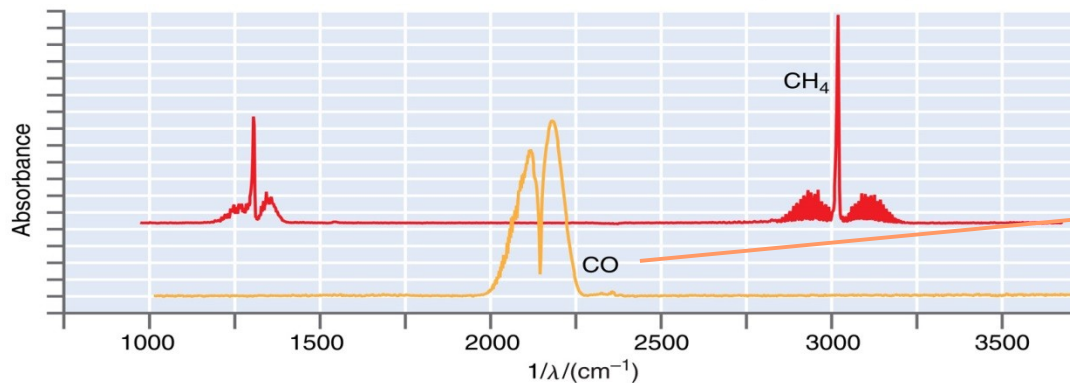
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$$\alpha = \sqrt{\frac{k}{2D_e}}$$

$$D_e = D_o + E_o = D_o + \frac{h\nu}{2} - \frac{(h\nu)^2}{16 D_e}$$

Niveles vibracionales para un oscilador cuántico con potencial de Morse

$$E_n = h\nu \left(n + \frac{1}{2} \right) - \frac{(h\nu)^2}{4D_e} \left(n + \frac{1}{2} \right)^2 \quad n = 0, 1, 2, 3, \dots$$



$$\Delta E = hc/\lambda = f(\nu, n, D_e)$$

Información estructural

Espectro IR de CO y CH₄ en fase gaseosa

Determinación de Estructura Molecular a partir de Espectroscopía vibracional y rotacional

TABLE 19.3 VALUES OF MOLECULAR CONSTANTS FOR SELECTED DIATOMIC MOLECULES

	$\tilde{\nu}$ (cm ⁻¹)	ν (s ⁻¹)	x_e (pm)	k (N m ⁻¹)	B (cm ⁻¹)	D_0 (kJ mol ⁻¹)	D_0 (J molecule ⁻¹)
H ₂	4401	1.32×10^{14}	74.14	575	60.853	436	7.24×10^{-19}
D ₂	3115	9.33×10^{13}	74.15	577	30.444	443	7.36×10^{-19}
¹ H ⁸¹ Br	2649	7.94×10^{13}	141.4	412	8.4649	366	6.08×10^{-19}
¹ H ³⁵ Cl	2991	8.97×10^{13}	127.5	516	10.5934	432	7.17×10^{-19}
¹ H ¹⁹ F	4138	1.24×10^{14}	91.68	966	20.9557	570	9.46×10^{-19}
¹ H ¹²⁷ I	2309	6.92×10^{13}	160.92	314	6.4264	298	4.95×10^{-19}
³⁵ Cl ₂	559.7	1.68×10^{13}	198.8	323	0.2440	243	4.03×10^{-19}
⁷⁹ Br ₂	325.3	9.75×10^{12}	228.1	246	0.082107	194	3.22×10^{-19}
¹⁹ F ₂	916.6	2.75×10^{13}	141.2	470	0.89019	159	2.64×10^{-19}
¹²⁷ I ₂	214.5	6.43×10^{12}	266.6	172	0.03737	152	2.52×10^{-19}
¹⁴ N ₂	2359	7.07×10^{13}	109.8	2295	1.99824	945	1.57×10^{-18}
¹⁶ O ₂	1580.	4.74×10^{13}	120.8	1177	1.44563	498	8.27×10^{-19}
¹² C ¹⁶ O	2170.	2.56×10^{13}	112.8	1902	1.9313	1076	1.79×10^{-18}

Source: Lide, D. R., Ed., *CRC Handbook of Chemistry and Physics*, 83rd Edition. CRC Press, Boca Raton, FL, 2003.

Reglas de Selección para transiciones vibracionales

Oscilador armónico: $\Delta v = \pm 1$

Oscilador anarmónico: $\Delta v = \pm 1, \pm 2, \pm 3, \dots$
sobretonos

Integral del momento dipolar de transición
entre los estados m y n

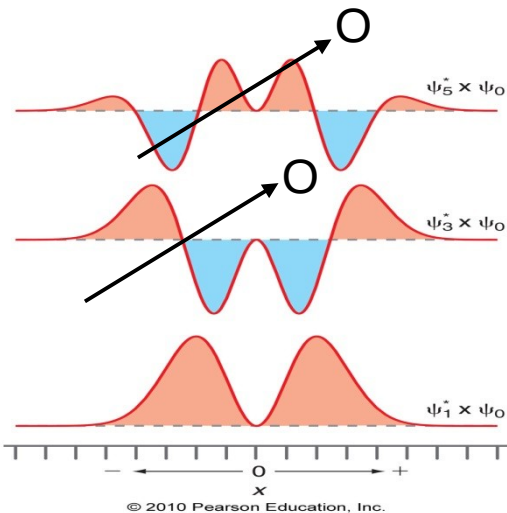
$$\mu_x^{mn} = \int \psi_m^*(x) \mu_x(x) \psi_n(x) dx \neq 0$$

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Obtención de los tránsitos permitidos
entre niveles vibracionales

$$\mu_x(x(t)) = \mu_{0x} + x(t) \left(\frac{d\mu_x}{dx} \right)_{x=0} + \dots$$

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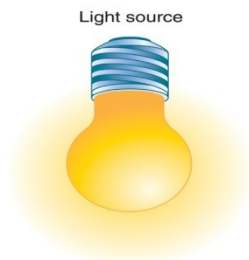
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$$\begin{aligned} \mu_x^{m0} &= A_m A_0 \mu_{0x} \int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) H_0(\alpha^{1/2}x) e^{-\alpha x^2} dx \\ &+ A_m A_0 \left[\left(\frac{d\mu_x}{dx} \right)_{x=0} \right] \int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) x H_0(\alpha^{1/2}x) e^{-\alpha x^2} dx \end{aligned}$$

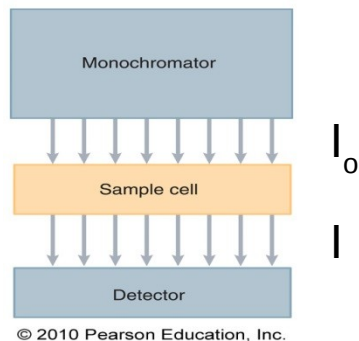
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$$n = 0 \rightarrow m = 2b + 1, \text{ for } b = 0, 1, 2, \dots$$

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Espectroscopia Infrarroja



$$dI(\lambda) = -\epsilon(\lambda)MI(\lambda) d\lambda$$

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coeficiente de absorción molar

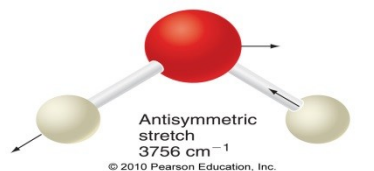
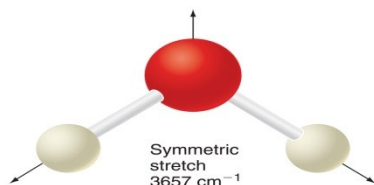
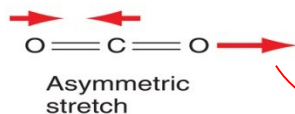
Ecuación de Lambert-Beer

$$\frac{I(\lambda)}{I_0(\lambda)} = e^{-\epsilon(\lambda)Ml}$$

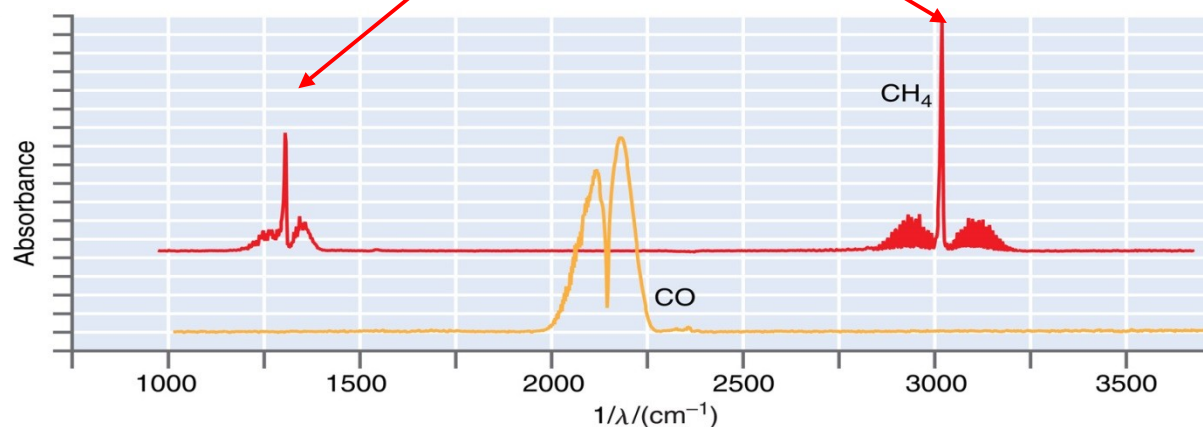
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CH₄ solo presenta 2 bandas en lugar de 9
la estructura de las bandas es debido a tránsitos rotacionales

Modos normales de vibración



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Espectro IR de CO y CH₄ en fase gaseosa

Group	Frequency (cm ⁻¹)	Group	Frequency (cm ⁻¹)
O—H stretch	3450–3650	C=O stretch	1650–1750
N—H stretch	3300–3500	C=C stretch	1620–1680
C—H stretch	2800–3000	C—C stretch	1200–1300
C—H bend	1450–1480	C—Cl stretch	600–800

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Espectroscopia Rotacional

$$E = \frac{\hbar^2}{2\mu r_0^2} J(J+1) = \frac{h^2}{8\pi^2 \mu r_0^2} J(J+1) = hcBJ(J+1)$$

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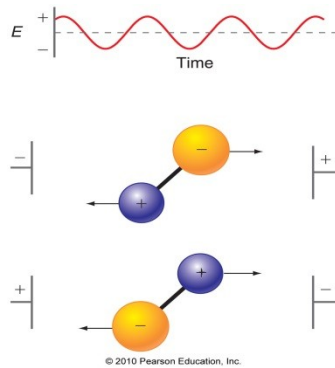
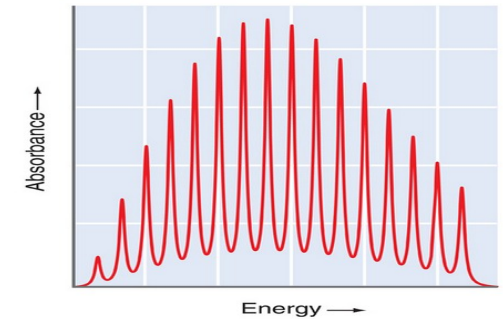
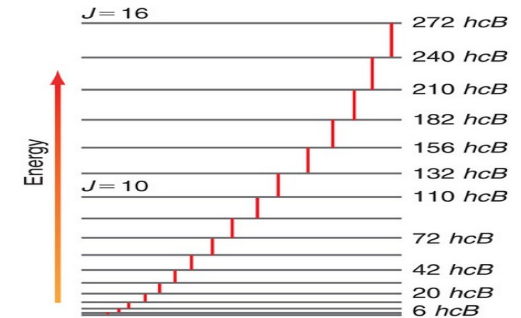


TABLE 19.5 FREQUENCIES NEEDED TO EXCITE VARIOUS ROTATIONAL TRANSITIONS

$J \rightarrow J'$	$\Delta\nu$	$\Delta(\Delta\nu)$
$0 \rightarrow 1$	$2cB$	$2cB$
$1 \rightarrow 2$	$4cB$	$2cB$
$2 \rightarrow 3$	$6cB$	$2cB$
$3 \rightarrow 4$	$8cB$	$2cB$
$4 \rightarrow 5$	$10cB$	$2cB$

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Rotación activa en espectroscopia de absorción rotacional (microondas)

$$\Delta E = E(J_{final}) - E(J_{initial})$$

for $\Delta J = +1$

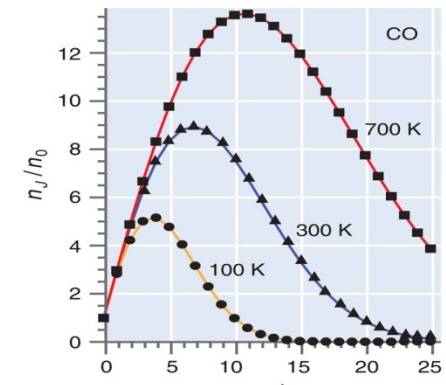
Regla de Selección

$$\Delta J = \pm 1$$

$$\begin{aligned} \Delta E_+ &= \frac{\hbar^2}{2\mu r_0^2} (J+1)(J+2) - \frac{\hbar^2}{2\mu r_0^2} J(J+1) \\ &= \frac{\hbar^2}{2\mu r_0^2} [(J^2 + 3J + 2) - (J^2 + J)] = \frac{\hbar^2}{\mu r_0^2} (J+1) \\ &= 2hcB(J+1) \quad \text{and for } \Delta J = -1 \end{aligned}$$

$$\begin{aligned} \Delta E_- &= \frac{\hbar^2}{2\mu r_0^2} (J-1)J - \frac{\hbar^2}{2\mu r_0^2} J(J+1) \\ &= \frac{\hbar^2}{2\mu r_0^2} [(J^2 - J) - (J^2 + J)] = -\frac{\hbar^2}{\mu r_0^2} J = -2hcBJ \end{aligned}$$

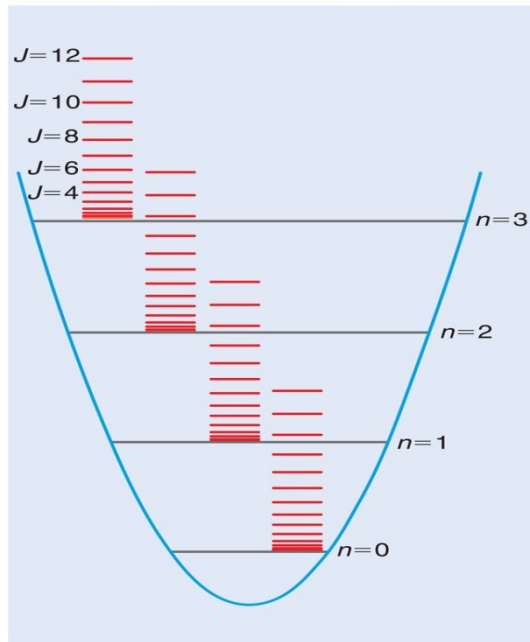
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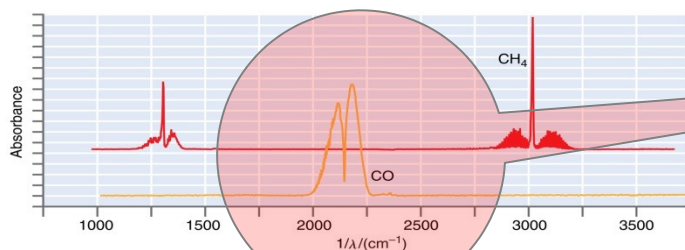
$$\frac{n_J}{n_0} = \frac{g_J}{g_0} e^{-(E_J - E_0)/kT} = (2J+1) e^{-\hbar^2 J(J+1)/(2IkT)}$$

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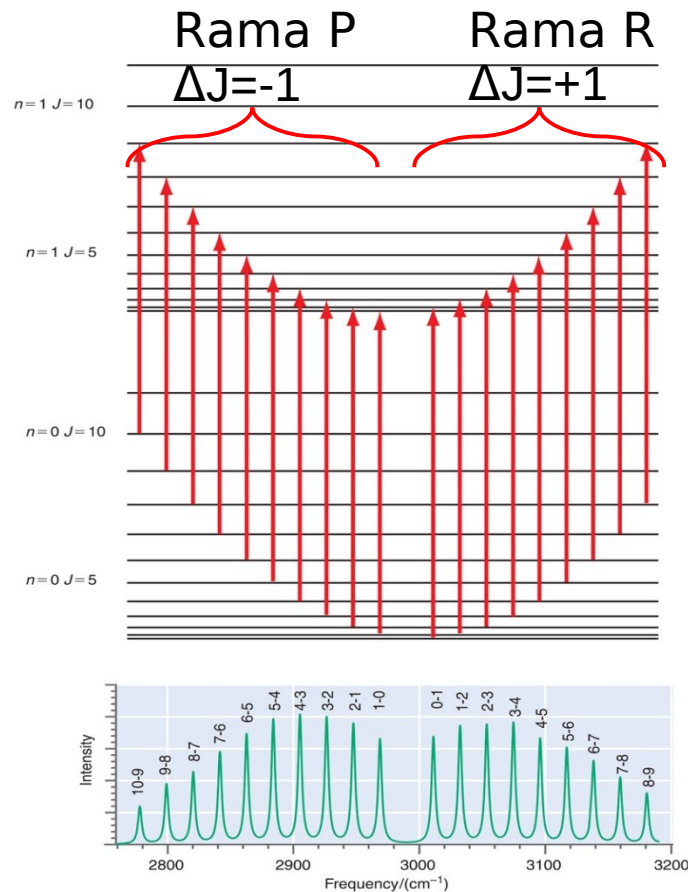
Espectro roto-vibracional



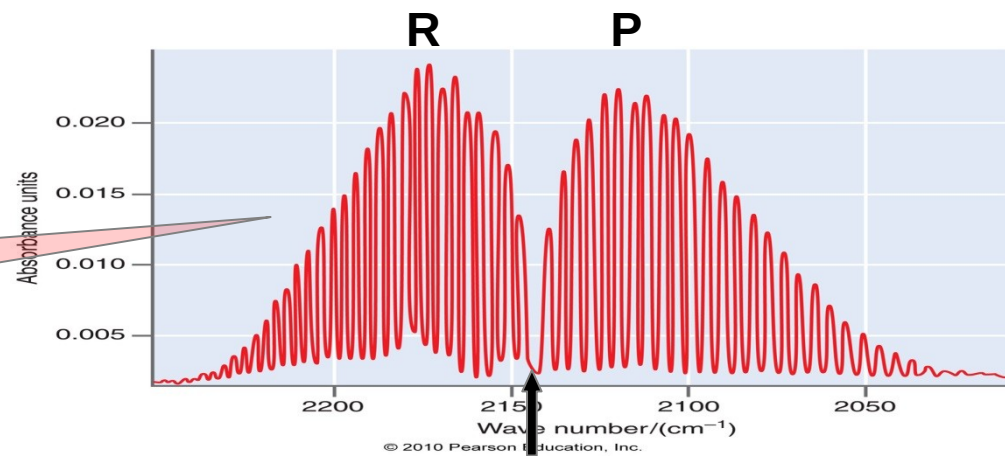
vibro-rotación



Espectro IR de CO



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origen de la banda