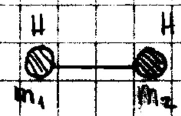
Serie 6 | Espectroscopía Molecular | HOJA | FECHA

A. Transiciones rotacionales

1.

$$B_v = \langle \Psi_v | \frac{1}{2\mu R^2} | \Psi_v \rangle$$

i. H_2



$\rightarrow m_1 = m_2 \equiv m \rightarrow \mu = \frac{m^2}{2m} = \frac{m}{2}$

$$B_0 = 60.853 \frac{1}{cm} \rightarrow 6085,3 \frac{1}{m} \qquad R = \sqrt{\frac{1}{2\mu B_0}} = \frac{1}{\sqrt{m \cdot B_0}}$$

$$E_v = \frac{J(J+1)h^2}{8\pi^2 I} \Rightarrow \qquad B_v = \frac{E_v}{hc} \Rightarrow$$

1 UMA $\rightarrow 1{,}66 \cdot 10^{-27}$ Kg
$1\ a_0 \rightarrow 5{,}29 \cdot 10^{-11}$ m

$$B_v^{(J)} = \frac{J(J+1)h}{8\pi^2 c I} = \frac{J(J+1)\hbar}{2\pi c\ 2\mu R^2}$$

MASA (H) $\rightarrow 1{,}0078$ UMA

con $J=0 \rightarrow$
$$B_v^{(0)} = \frac{\hbar}{(2\pi c)\,2\mu R^2}$$

$$R = \sqrt{\frac{\hbar}{2\pi c\ 2\mu B_v^0}}$$

$R = 7{,}41 \cdot 10^{-11}$ m

$$\boxed{R = 1{,}40\ a_0}$$

ii. N_2 $\qquad B_0 = 1{,}998 \frac{1}{cm} \rightarrow 199{,}8 \frac{1}{m}$

MASA (N) $\rightarrow 14{,}007$ UMA

$$R = \sqrt{\frac{\hbar}{2\pi c\ 2\mu B_v^0}}$$

NOTA
También
$$E_v = \frac{J(J+1)\hbar^2}{2I}$$

$R = 1{,}097 \cdot 10^{-10}$ m

$$\boxed{R = 2{,}07\ a_0}$$

2.

i) $J = 3 \rightarrow J = 4$

$$\Delta E = h\nu = \frac{J_f(J_f+1)h^2}{8\pi^2 I} - \frac{J_i(J_i+1)h^2}{8\pi^2 I} = \frac{h^2}{8\pi^2 I}(20-12) = \frac{h^2}{\pi^2 I}$$

$$\frac{\tilde{m}_N^{14} \cdot \tilde{m}_O^{16}}{m_N + m_O} = \mu \qquad \nu = \frac{h}{\pi^2 I}$$

$$I = \mu R^2 = (7{,}46\ \text{uma}) \cdot (1{,}15\ 10^{-10}\text{m})^2 = 1{,}64\ 10^{-46}\ m^2 Kg$$

$$\boxed{\nu = 4{,}09 \cdot 10^{11}\ \frac{1}{s}}$$

(Anda entre las microondas y el infrarrojo)

NOTA

2.

$\sim 12 \quad \sim 16$ (UMA)

$\mu = 6{,}857 \cdot 1{,}66 \cdot 10^{-27}\,kg$

$R^2 = 1{,}27 \cdot 10^{-20}\,m^2$

$$\Delta E_{2\to 3} = h\,\nu = \frac{h^2}{8\pi^2 I}\left[J_f(J_f+1) - J_i(J_i+1)\right] = \frac{6h^2}{8\pi^2 I}$$

$$\boxed{\Delta\nu = 3{,}48 \cdot 10^{11}\,\frac{1}{s}}$$

3.

$$\tilde{k} = \frac{1}{\lambda} = \frac{\nu}{c} \rightarrow \tilde{k}\,c = \nu$$

$c = \lambda\,\nu$

$\sim 1 \quad \sim 81$ (UMA)

$J=3 \leftarrow 2$ es $\Delta\nu = \dfrac{6h}{8\pi^2 I}$

$$\tilde{k} = \frac{6h}{8c\pi^2 I} = \frac{3}{4c}\frac{h}{\pi^2 I}$$

$$I = \frac{3h}{4\pi^2 c\,\tilde{k}} = 2{,}64 \cdot 10^{-47}\,m^2\,kg$$

$$I = \mu\,R^2 \rightarrow R = \sqrt{\frac{I}{\mu}}$$

$$R = \sqrt{1{,}61 \cdot 10^{-20}}$$

$$R = 1{,}27 \cdot 10^{-10}$$

$$\boxed{R = 2{,}4\,a_0}$$

1,4114

4.

$$B_\nu = \frac{E_\nu}{hc} = \frac{h}{4\pi c(\mu R^2)} \rightarrow R = \left(\frac{h}{4\pi c\,\mu\,B_\nu^{(0)}}\right)^{1/2}$$

$11{,}42\,\dfrac{1}{m}$

$$\mu = \left(\frac{127 \cdot 35}{127+35}\right) 1{,}66 \cdot 10^{-27}\,kg$$

$$\mu = 4{,}55 \cdot 10^{-26}\,kg$$

$R = 2{,}32 \cdot 10^{-10}\,m$

$$\boxed{R = 4{,}38\,a_0}$$

5.

$\sim 1 \; \sim 12 \; \sim 14$

HCN

(1) (4) (5)

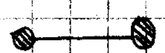
H· ·C· :N·

(monov.) (tetrav.) (triv.)

C-N será el enlace mayor debido al mayor # de electrones que debe acomodar.

H ×C ××× N

$H - C \equiv N$



Las constantes son para cada enlace

$$B_\nu^{(J)} = \frac{E_\nu}{h} = \frac{J(J+1)h}{8\pi^2 I} \rightarrow$$

$$B_\nu^{(0)} = \frac{h}{8\pi^2 \mu R^2}$$

Enlaces

		μ [UMA]				
mayor R	(C-N)	6,461 uma	$\rightarrow$	$B_\nu^{(0)}$ menor	$\rightarrow$	$B_\nu^{(0)} = 36{,}208$ GHz
menor R	H-C	0,923 uma	$\rightarrow$	$B_\nu^{(0)}$ mayor	$\rightarrow$	$B_\nu^{(0)} = 44{,}316$ GHz

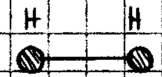
$$R_{(C-N)} = \left(\frac{h}{8\pi^2\mu B_\nu^{(0)}}\right)^{1/2} \qquad R_{(H-C)} = \left(\frac{h}{8\pi^2\mu B_\nu^{(0)}}\right)^{1/2}$$

$R = 1{,}32 \cdot 10^{-10}\,m$ $\qquad$ $R = 3{,}52 \cdot 10^{-10}$

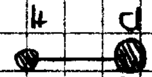
$$\boxed{R = 2{,}51\,a_0} \qquad \boxed{R = 6{,}65\,a_0}$$

NOTA

6.

$H_2 \rightarrow$ 

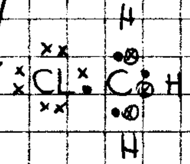
monopolo $\neq 0$
dipolo $= 0$

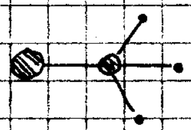
$HCL \rightarrow$ 

monopolo $= 0$
dipolo $\neq 0$

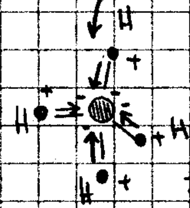
$H^+ \; CL^-$

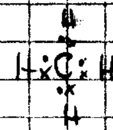
CH_3CL





CH_4

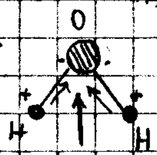




monopolo $= 0$
dipolo $= 0$

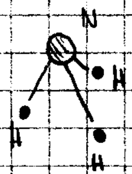
Por la simetría parecería que no hay dipolo eléctrico

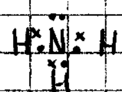
H_2O



monopolo $= 0$
hay dipolo $\neq 0$

NH_3





N_2O

monopolo $= 0$
dipolo $= 0$

Hay que mirar si

H_2	HCL	CH_4	CH_3CL	H_2O
→ No puede tener	Puede tener	No Puede tener	Puede tener	Puede tener

NH_3	N_2O
Puede tener	No puede tener

NOTA

		HOJA
		FECHA

2. $U(\rho) = D_e\left(1-e^{-\varkappa\rho}\right)^2 \qquad \rho = R - R_{eq}$

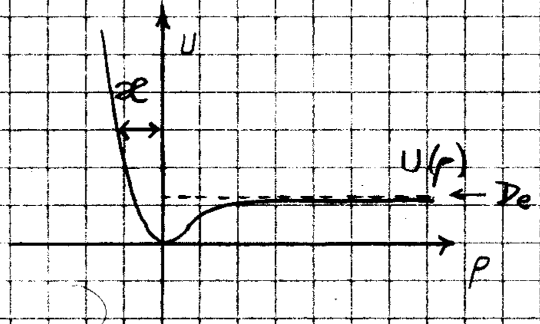
i.

$$\frac{\partial U}{\partial \rho} = D_e\, 2\left(1-e^{-\varkappa\rho}\right)\left(-e^{-\varkappa\rho}\right)(-\varkappa) = 2\varkappa D_e\left(e^{-\varkappa\rho} - e^{-2\varkappa\rho}\right)$$

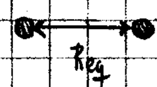
$$\frac{\partial U}{\partial \rho} = 0 = 2\varkappa D_e\left(e^{-\varkappa\rho} - e^{-2\varkappa\rho}\right)$$

$$e^{-\varkappa\rho} = e^{-2\varkappa\rho} \Leftrightarrow \boxed{\rho = 0}$$

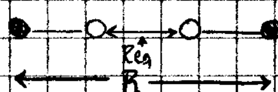
Tendremos un mínimo para la función de Morse cuando $R = R_{eq}$



$\varkappa$ está asociado al retorno a la posición de equilibrio
D_e está asociada a la disociación bajo este potencial

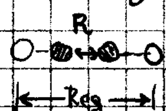


Cuando $\rho > 0$ estamos viendo que $R > R_{eq}$ y entonces las partículas se separan:



se tiende al potencial de disociación (cuando comienza a verse como un estado NO ligado). D_e es el límite del potencial cuando $\rho \to \infty$

Cuando $\rho < 0$ las partículas se juntan $R < R_{eq}$ y comienza a actuar la re-



pulsión que es casi como una pared infinita. $\varkappa$ está asociada a esta repulsión.

ii.

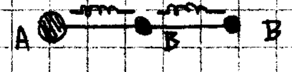
NOTA

4.

a) AB_2 → Lineal → ①

no tiene $\vec{\mu}$ (dipolar) (x simetría)
No será activa en el infrarojo

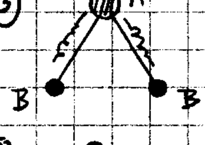
②



tiene momento dipolar ⇒ puede ser activa en el infrarojo

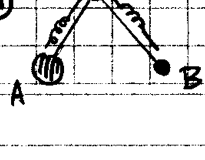
b) AB_2 → angular

③



Tiene momento dipolar ⇒ pueden ser activas en el infrarojo

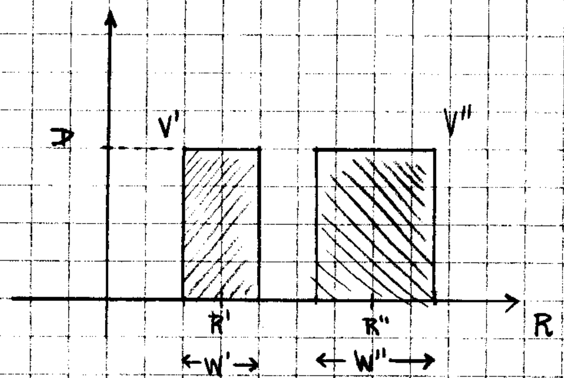
④



NOTA

C. Transiciones electrónicas

1.



$$V' = \begin{cases} D & \text{si } R \in \left(R' - \frac{W'}{2}, R' + W'\right) \\ 0 & \text{si } R \notin \end{cases}$$

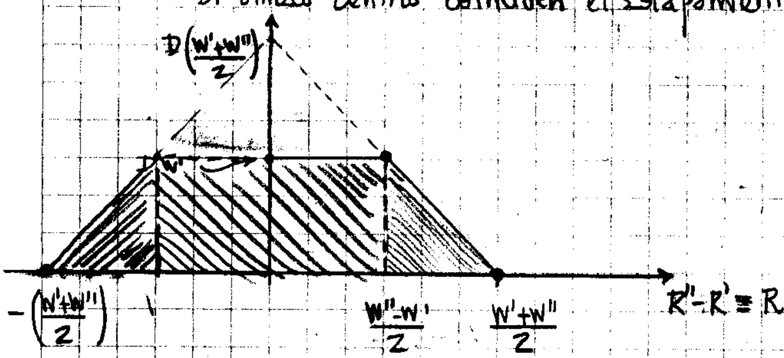
$$V'' = \begin{cases} D & \text{si } R \in \left(R'' - \frac{W''}{2}, R'' + \frac{W''}{2}\right) \\ 0 & \text{si } R \notin \end{cases}$$

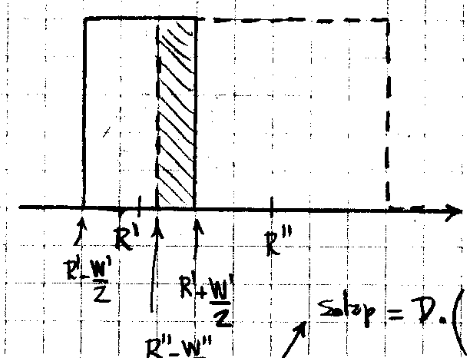
$W'' > W'$

Hay solapamiento si $R''-R' < \frac{W'}{2} + \frac{W''}{2} = \frac{W'+W''}{2}$

$S^{e'e''}_{v'v''} = \int_{-\infty}^{+\infty} \psi^{v'} \cdot \psi^{v''} \, dR$ → Lo podemos pensar como el área del solapamiento

Si ambos centros coinciden el solapamiento es $D.W'$





$S_{olap} = D.\left(R' + \frac{W'}{2} - R'' - \frac{W''}{2}\right.$

$S_{olap} = D.\left(R'-R'' + \frac{W'+W''}{2}\right.$

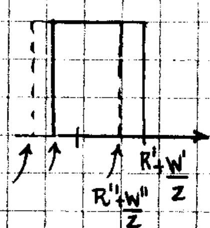
$S_{olap} = -D.R + D\left(\frac{W'+W''}{2}\right.$

hasta que

$R''-\frac{W''}{2} = R'-\frac{W'}{2}$

$R''-R' = \frac{W''-W'}{2}$

$-D\left(R'-R'' + \frac{W'+W''}{2}\right)$



$D.W' + D\left(R' + \frac{W'}{2} - \left(R'' + \frac{W''}{2}\right)\right) - D\left(R' + \frac{W'}{2} - (R''\right.$

$D.W' + D\left(R + \left(\frac{W''-W'}{2}\right)\right) + D\left(R + \frac{W''+W'}{2}\right)$ $-D\left(R'-R'' + \frac{W'+W''}{2}\right)$

$S_{olap} = D.R + D\left(\frac{W''-W'}{2}\right) + D.W'$

$D.R + D\left(\frac{W''+W'}{2}\right)$