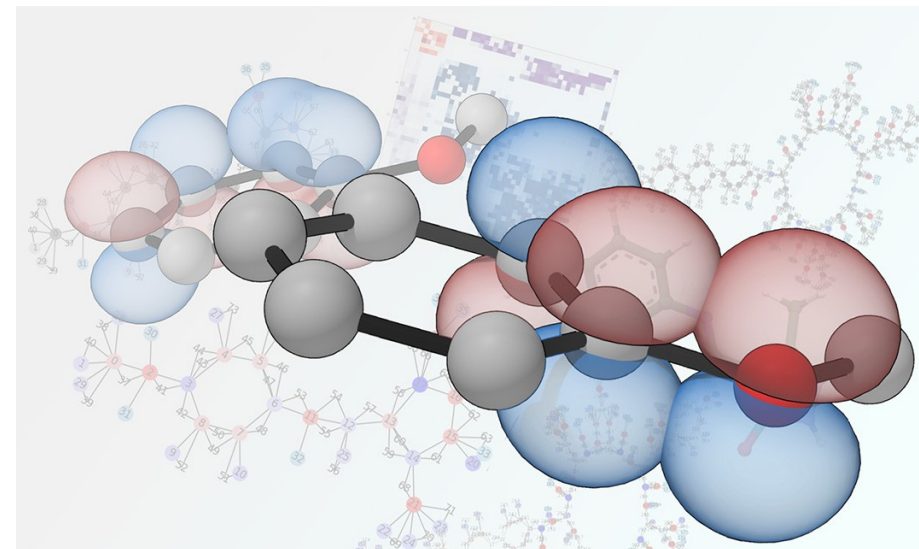


Aula 03 – Termodinâmica Molecular

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$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$$

$$|\Psi\rangle = |\psi\rangle e^{-iEt/\hbar}$$

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

Ensemble Canônico

Função de partição canônica

$$Q(N, V, T) = \sum_i e^{-\beta \epsilon_i} \quad \text{com} \quad \beta = \frac{1}{k_B T}$$

Quantidades Termodinâmicas

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

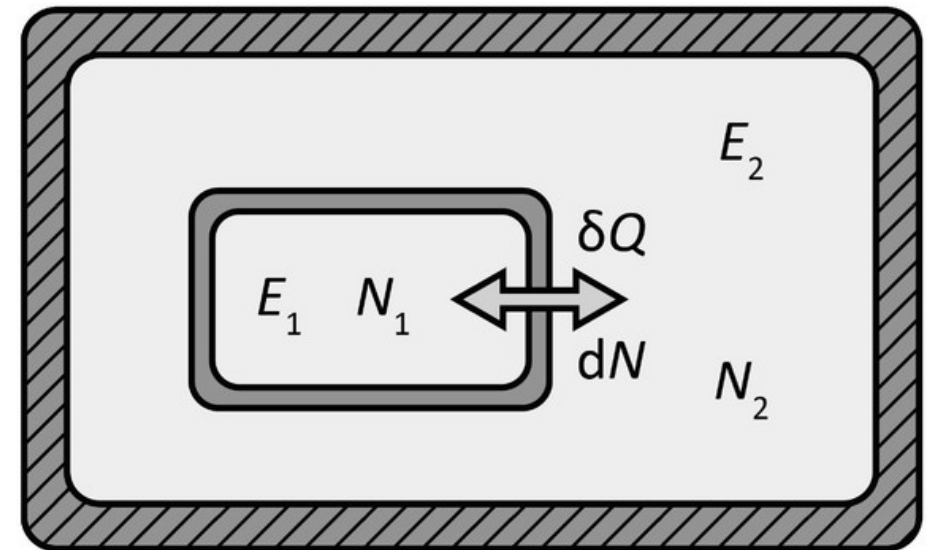
$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

$$H = U + PV$$

$$G = H - TS$$

Energia de Helmholtz

$$F = -k_B T \ln Q$$



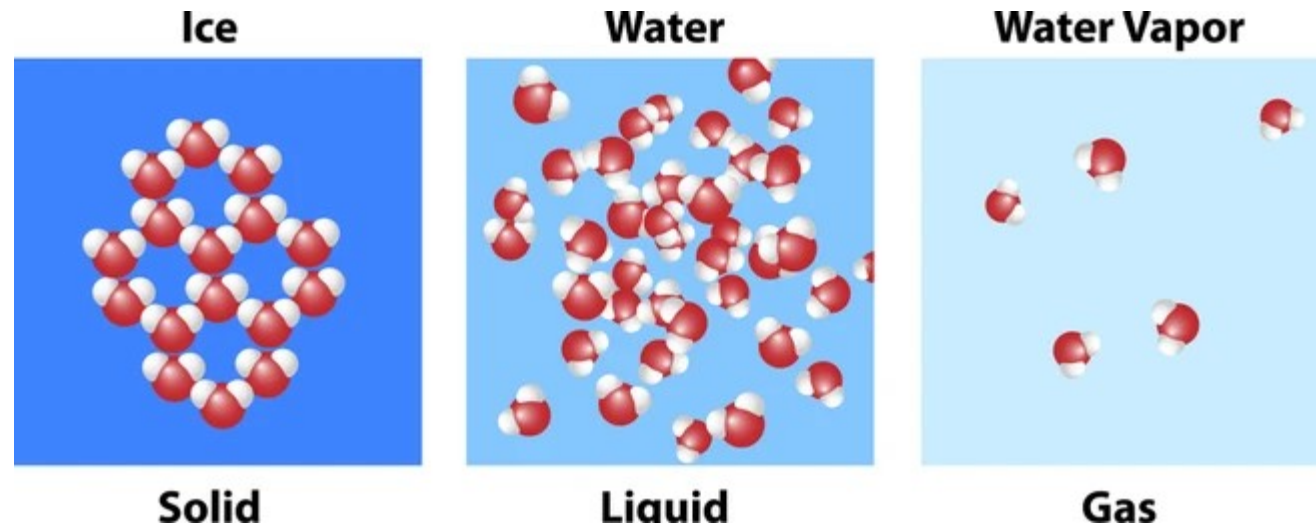
Aproximação de Gás Ideal

Moléculas não interagem entre si

$$Q(N, V, T) = \frac{1}{N!} \sum_i e^{-\beta[\epsilon_1 + \epsilon_2 + \dots + \epsilon_N]_i}$$
$$= \frac{[q(V, T)]^N}{N!}$$

Função de partição molecular

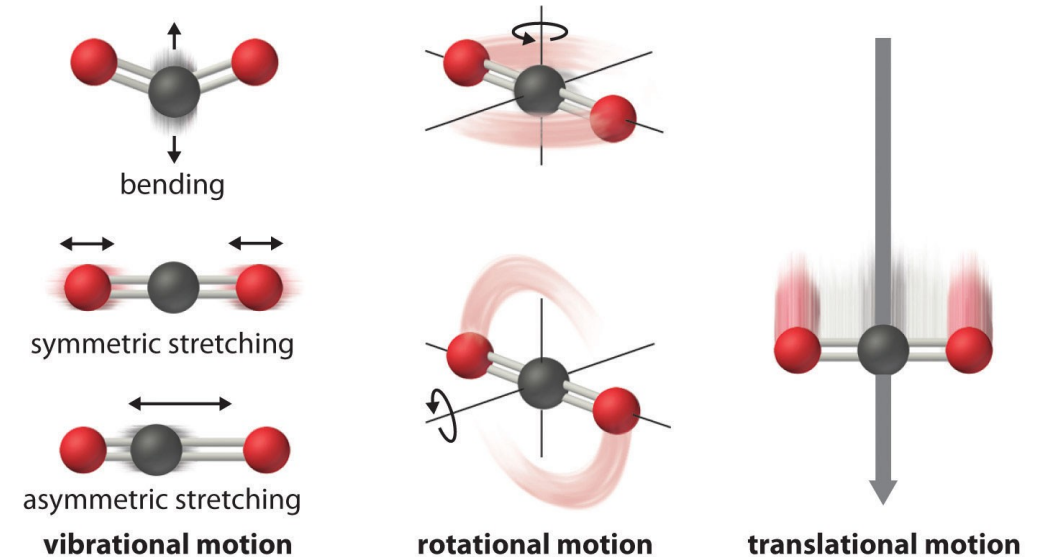
$$q(V, T) = \sum_i e^{-\beta\epsilon_i}$$



Separando Energias

Separação em auto-estados de energia

$$q(V, T) = \sum_{\mu}^{\text{energias}} e^{-\beta[\epsilon_{\text{trans}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{elec}}]_{\mu}}$$



$$q(V, T) = \left[\sum_i^{\text{trans}} e^{-\beta\epsilon_i} \right] \left[\sum_j^{\text{rot}} e^{-\beta\epsilon_j} \right] \left[\sum_k^{\text{vib}} e^{-\beta\epsilon_k} \right] \left[\sum_l^{\text{elec}} e^{-\beta\epsilon_l} \right]$$

Termodinâmica

$$\ln[Q(N, V, T)] = \ln\left\{ \frac{[q_{\text{trans}}(V, T)q_{\text{rot}}(V, T)q_{\text{vib}}(V, T)q_{\text{elec}}(V, T)]^N}{N!} \right\}$$

$$\begin{aligned} \ln[Q(N, V, T)] \approx & N \ln[q_{\text{trans}}(V, T)] + N \ln[q_{\text{rot}}(V, T)] \\ & + N \ln[q_{\text{vib}}(V, T)] + N \ln[q_{\text{elec}}(V, T)] - N \ln N + N \end{aligned}$$

Aproximação de Stirling

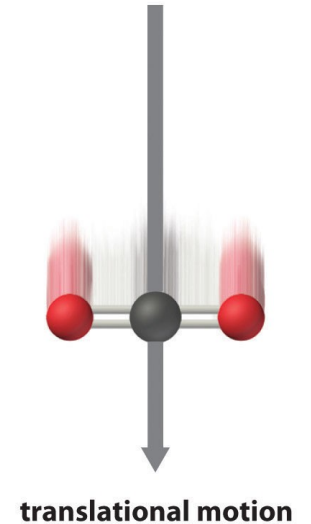
Função de Partição de Translação

$$q_{\text{trans}}(V, T) = \sum_i^{\text{trans}} e^{-\beta \epsilon_i}$$
$$= \frac{1}{h^3} \iint e^{-\beta \mathbf{p}^2 / 2M} d\mathbf{p} d\mathbf{r}$$

$$q_{\text{trans}}(V, T) = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V \longrightarrow$$

$$\frac{U_{\text{trans}}}{N} = \frac{3}{2} k_B T$$

$$\frac{S_{\text{trans}}}{N k_B} = \left[\ln q_{\text{trans}} + \frac{3}{2} \right]$$



Função de Partição de Rotação

$$q_{\text{rot}}(V, T) = \sum_j^{\text{rot}} e^{-\beta \epsilon_j}$$

$$= \sum_{j=0}^{\infty} g_j e^{-\beta \frac{\hbar^2 j(j+1)}{2I_{\text{eff}}}}$$

degenerescência

$$g_j = 2j + 1$$

$$q_{\text{rot}}(V, T) = \pi^{1/2} \left(\frac{8\pi^2 k_B T I_{\text{eff}}}{h^2} \right)^{3/2}$$



$$\frac{U_{\text{rot}}}{N} = \frac{d_{\text{rot}}}{2} k_B T$$

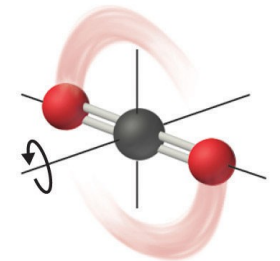
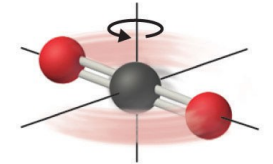
$$\frac{S_{\text{rot}}}{N k_B} = \left[\ln q_{\text{rot}} + \frac{d_{\text{rot}}}{2} \right]$$

Graus de liberdade de rotação

$$I_{\text{eff}} = \frac{(I_A I_B I_C)^{1/3}}{\sigma}$$

Mom. De inércia eixos principais

Número de simetria rotacional
(Table 10.1 - Cramer)

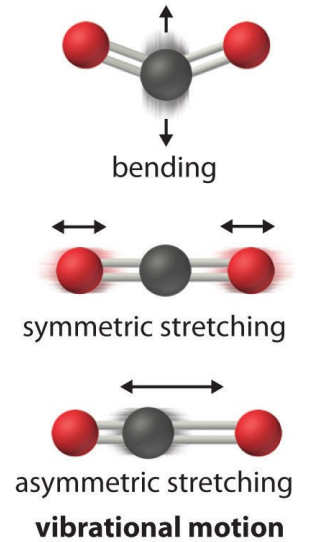


rotational motion

Função de Partição de Vibração

$$q_{\text{vib}}(V, T) = \sum_k^{\text{vib}} e^{-\beta \epsilon_k}$$

$$= \prod_{k=1}^{3M-3-d_r} \sum_{n_k=0}^{\infty} e^{-\beta \hbar (n_k + \frac{1}{2}) \omega_k}$$



$$q_{\text{vib}}(V, T) = \prod_{k=1}^{3M-3-d_r} \frac{e^{-\frac{1}{2}\beta \hbar \omega_k}}{(1 - e^{-\beta \hbar \omega_k})}$$

$$\xrightarrow{\quad} \frac{U_{\text{vib}}}{N} = \sum_{k=1}^{3M-3-d_r} \hbar \omega_k \left[\frac{1}{2} + \frac{e^{-\beta \hbar \omega_k}}{(1 - e^{-\beta \hbar \omega_k})} \right]$$

$$\frac{S_{\text{vib}}}{N k_B} = \sum_{k=1}^{3M-3-d_r} \left[\frac{1}{T} \frac{\hbar \omega_k e^{-\beta \hbar \omega_k}}{(1 - e^{-\beta \hbar \omega_k})} - \ln(1 - e^{-\beta \hbar \omega_k}) \right]$$

Função de Partição Eletrônica

$$q_{\text{ele}}(V, T) = \sum_l^{\text{ele}} e^{-\beta \epsilon_l}$$

Degenerescência de spin eletrônico

$$= e^{-\beta \epsilon_0} [g_0 + g_1 e^{-\beta \Delta \epsilon_1} + \dots]$$

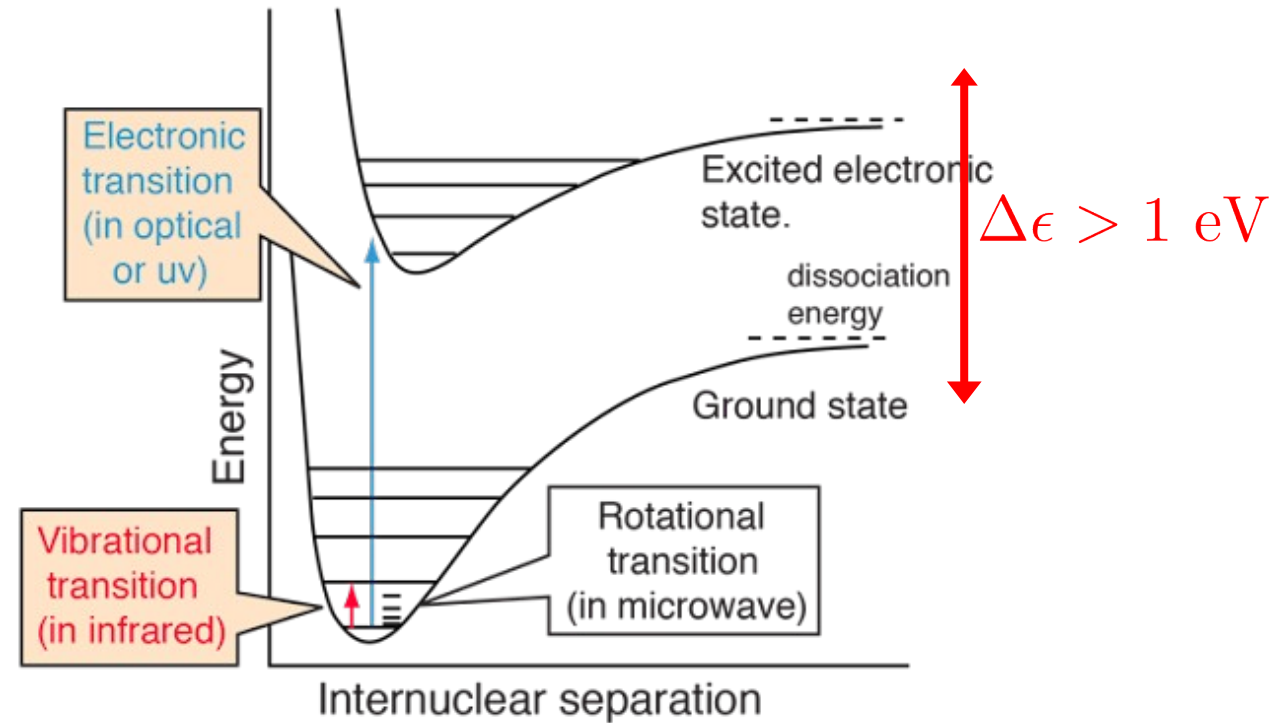
$$k_B T \approx 25 \text{ meV} (300 \text{ K})$$

$$e^{-\beta \Delta \epsilon_i} \ll 1$$

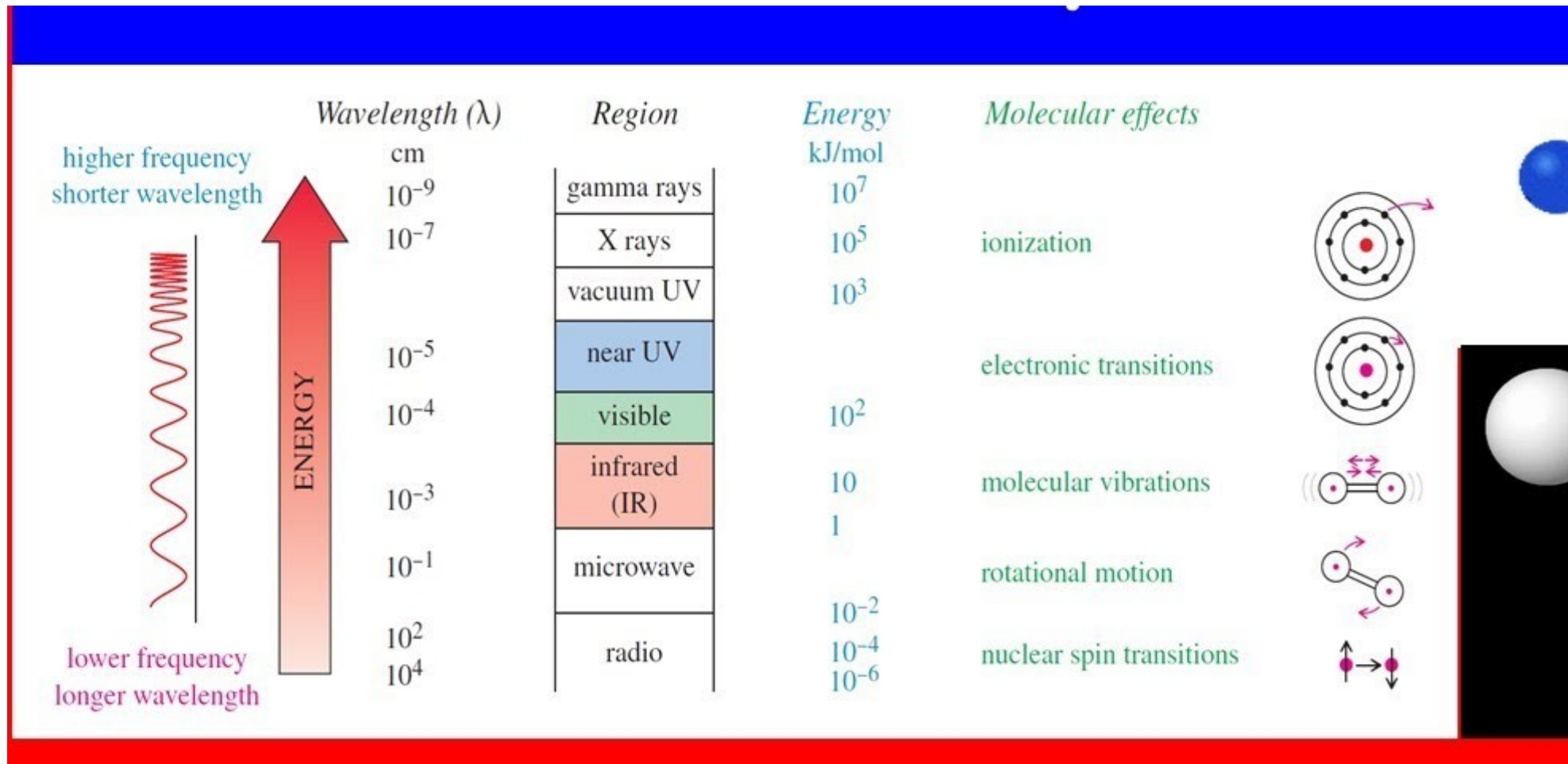
$$q_{\text{ele}}(V, T) \approx (2s + 1) e^{-\beta \epsilon_0}$$

$$E_{\text{ele}} = N \epsilon_0$$

$$S_{\text{ele}} = N k_B \ln(2s + 1)$$



Espectroscopia Molecular



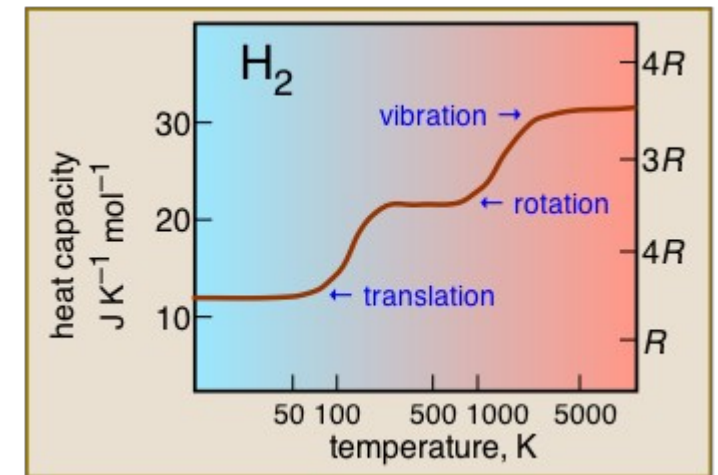
Funções Termodinâmicas

$$\frac{U}{N} = \frac{3}{2}k_B T + \frac{d_{\text{rot}}}{2}k_B T + \sum_{k=1}^{3M-3-d_{\text{rot}}} \hbar\omega_k \left[\frac{1}{2} + \frac{e^{-\beta\hbar\omega_k}}{(1 - e^{-\beta\hbar\omega_k})} \right] + \epsilon_0$$

$$\lim_{T \rightarrow 0} \frac{U}{N} = \sum_{k=1}^{3M-3-d_r} \frac{1}{2} \hbar\omega_k + \epsilon_0$$

Energia do estado
fundamental eletrônico

ZVPE
(Zero Vibrational Point Energy)



$$\frac{C_V}{Nk_B} = \left(\frac{\partial(U/Nk_B)}{\partial T} \right)_{N,V} = \frac{3}{2} + \frac{d_{\text{rot}}}{2} + \sum_{k=1}^{3M-3-d_{\text{rot}}} \left(\frac{\hbar\omega_k}{k_B T} \right)^2 \frac{e^{\beta\hbar\omega_k}}{(1 - e^{\beta\hbar\omega_k})^2}$$