

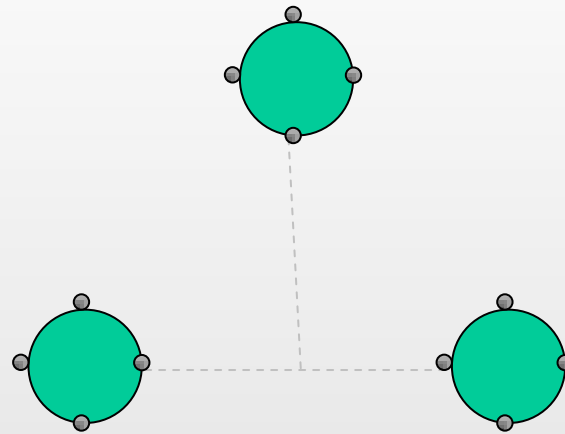
# *Dinámica No Lineal de Vibraciones Moleculares*

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Grupo de Sistemas Complejos

Universidad Politécnica de Madrid (UPM)

# SISTEMA MOLECULAR



# SISTEMA MOLECULAR

## Aproximación de Born-Oppenheimer

$$\hat{H}(\vec{r}, \vec{R})\Psi(\vec{r}, \vec{R}) = E_{TOTAL}\Psi$$

$$[\cancel{\hat{T}_N(\vec{R})} + \hat{H}_{el}(\vec{r}, \vec{R})]\cancel{\phi_N(\vec{R})}\Psi_{el}(\vec{r}, \vec{R}) = E_T \cancel{\phi_N}\Psi_{el}$$

$\underbrace{E_{el} + E_N}_{E_T}$

$$\hat{H}_{el}\Psi_{el}(\vec{r}, \vec{R}) = E_{el}\Psi_{el}$$

$$[\hat{T}_N(\vec{R}) + E_{el}(\vec{R})]\phi_N(\vec{R}) = E_T\phi_N$$

# SISTEMA MOLECULAR

## ESTUDIO DINÁMICO POR MECÁNICA CLÁSICA

**Vibraciones Moleculares**



**Vibraciones de los núcleos**

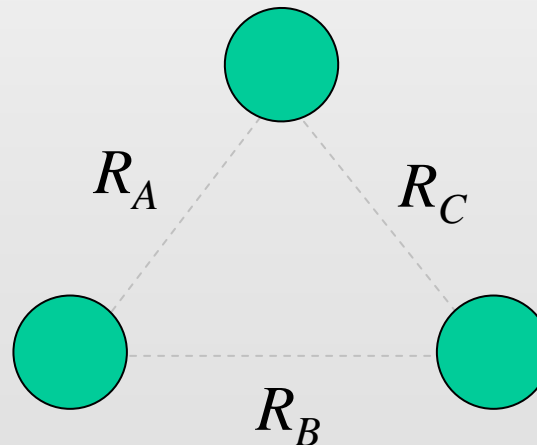
# SISTEMA MOLECULAR

## ESTUDIO DINÁMICO POR MECÁNICA CLÁSICA

**Vibraciones Moleculares**



**Vibraciones de los núcleos**

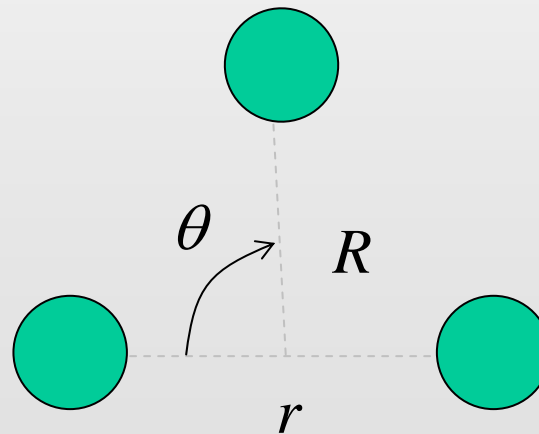


## ESTUDIO DINÁMICO POR MECÁNICA CLÁSICA

**Vibraciones Moleculares**

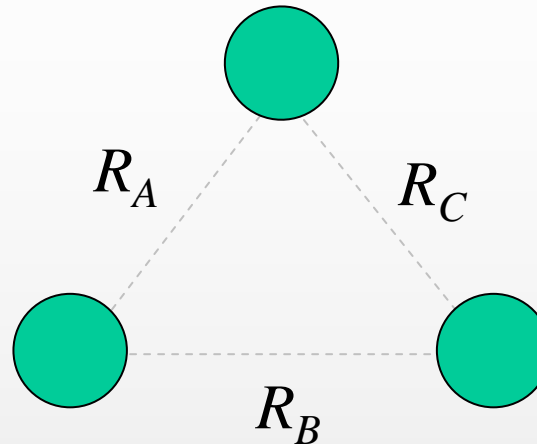


**Vibraciones de los núcleos**



# SISTEMA MOLECULAR

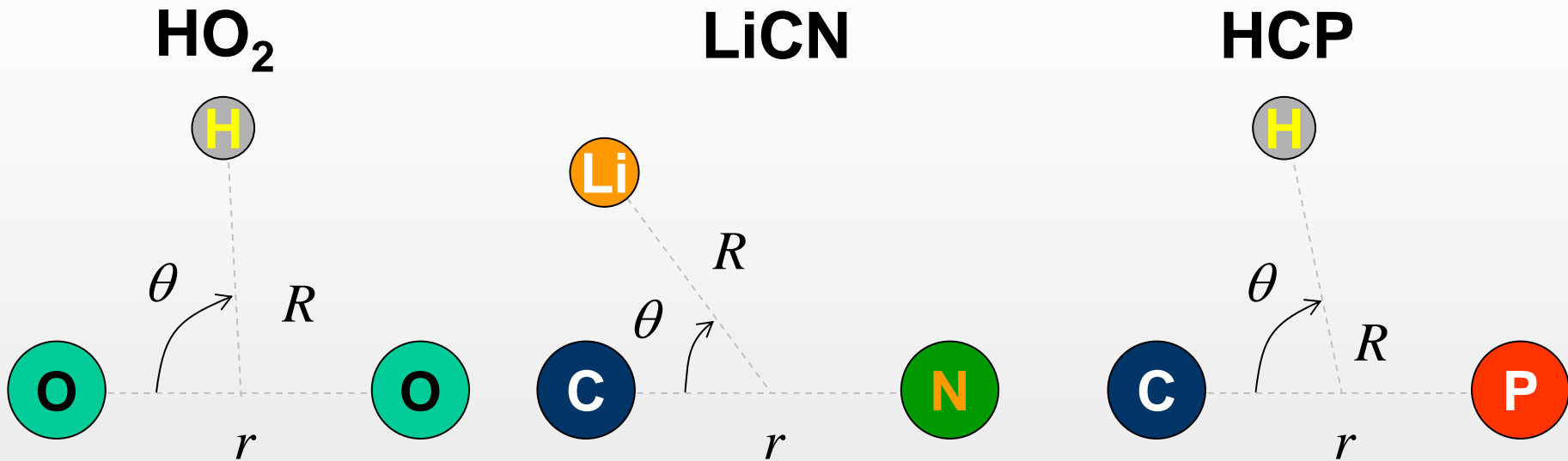
## Energía Potencial



$$\vec{R} = R(R_A, R_B, R_C)$$

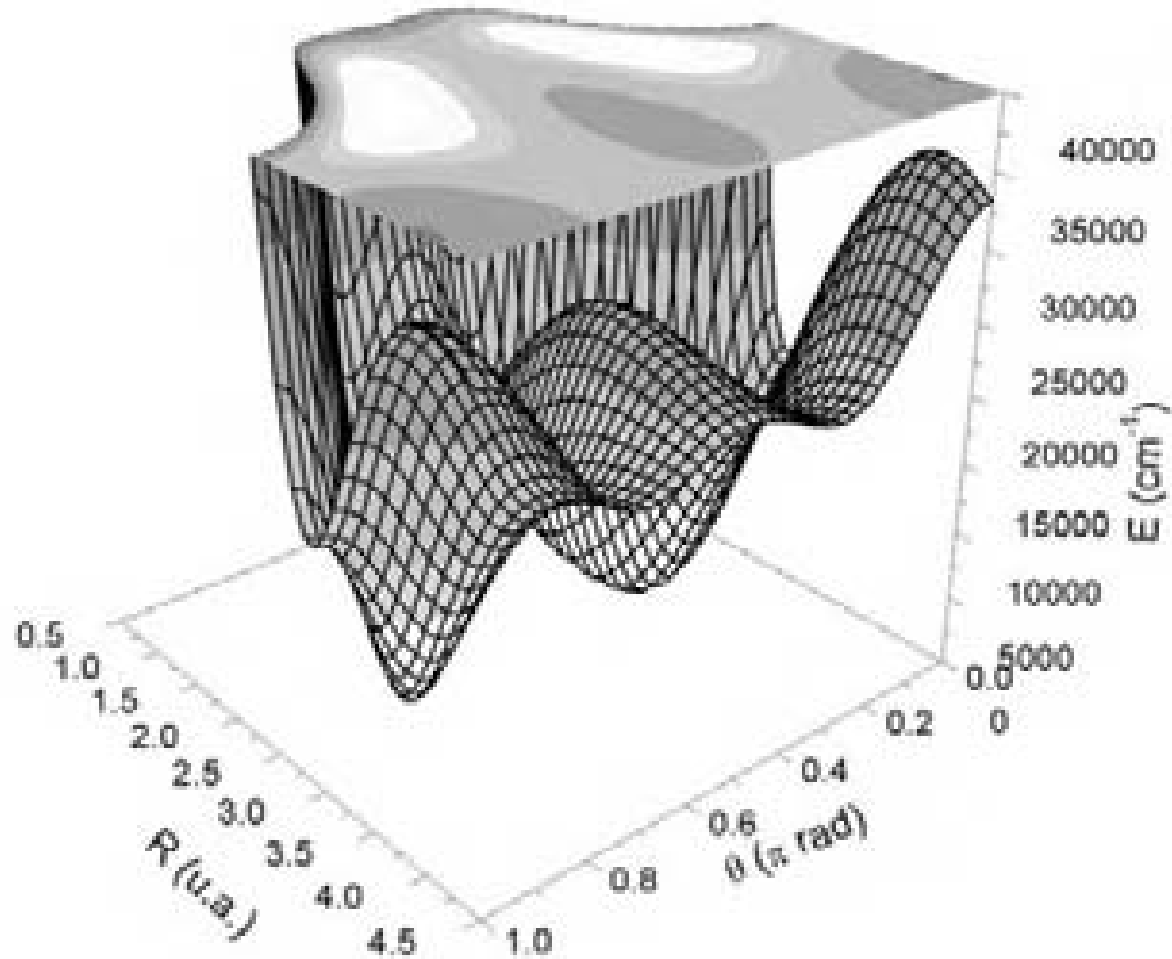
$$V_{ABC}(\vec{R}) = \sum_{i=1}^3 \left[ V_{AB, HF}^{(2)}(R_i) + V_{AB, corr}^{(2)}(R_i) \right] + V_{ABC, HF}^{(3)}(\vec{R}) + V_{ABC, corr}^{(3)}(\vec{R})$$

**Interacciones de dos cuerpos**    **Interacciones de tres cuerpos**

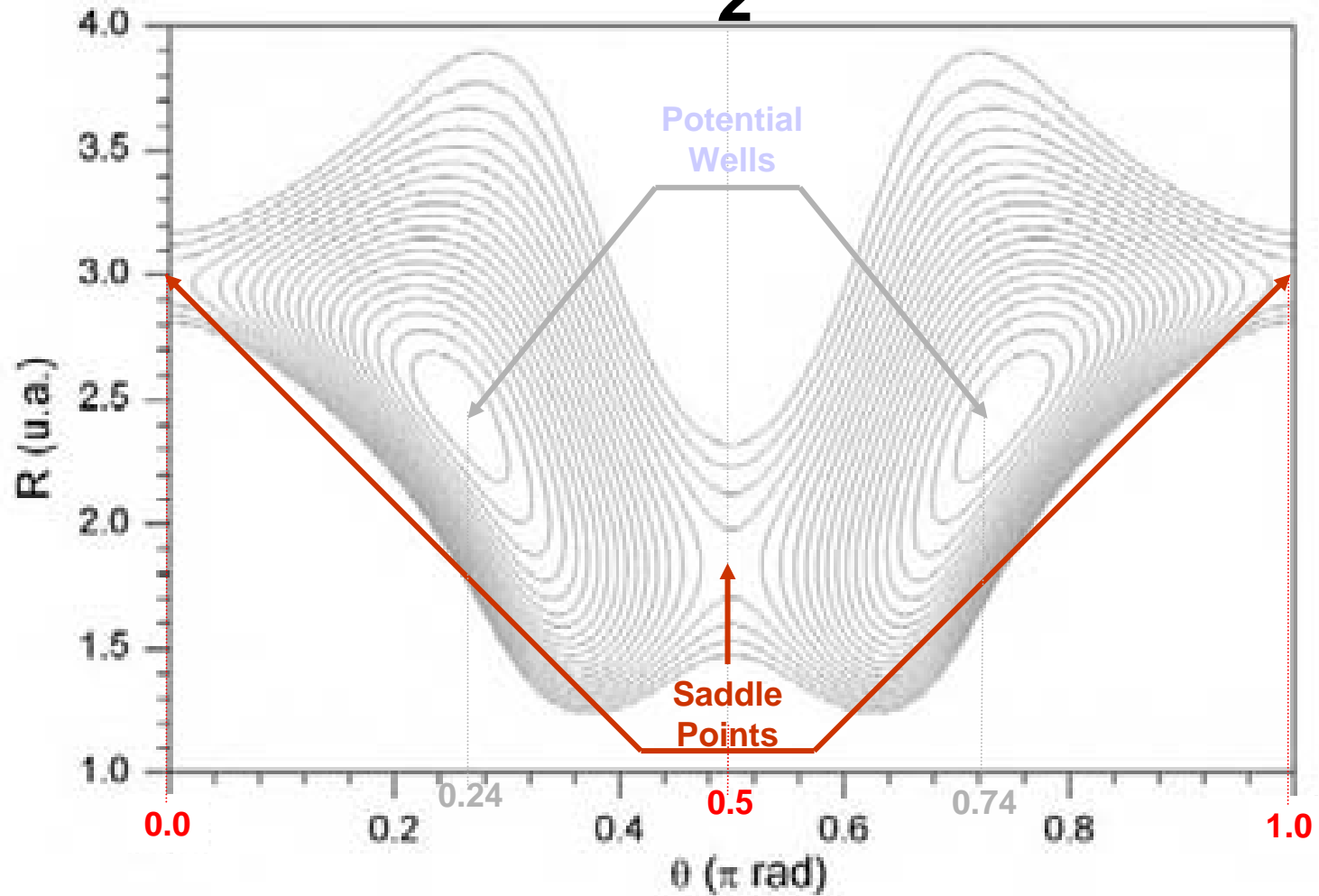




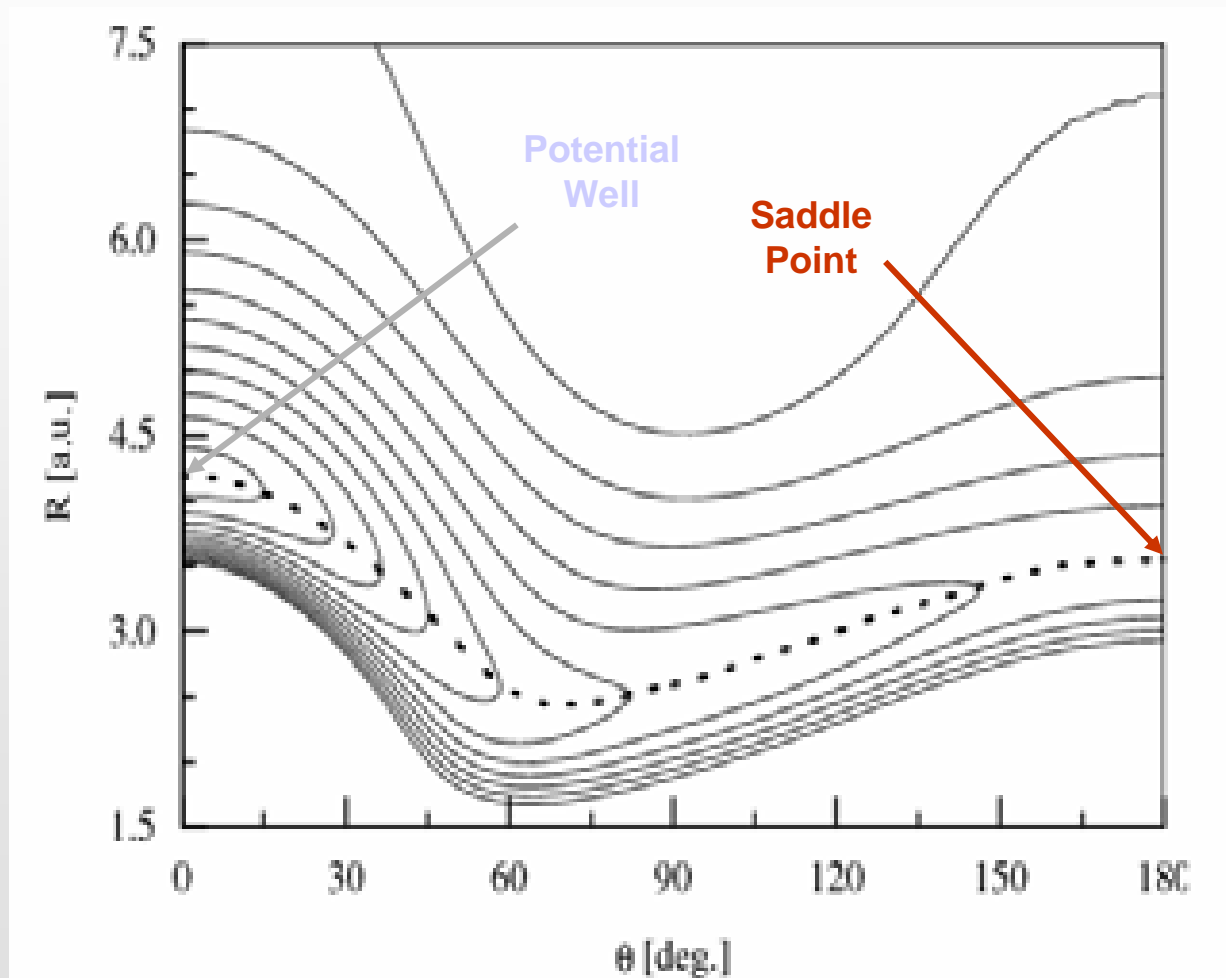
# HO<sub>2</sub>



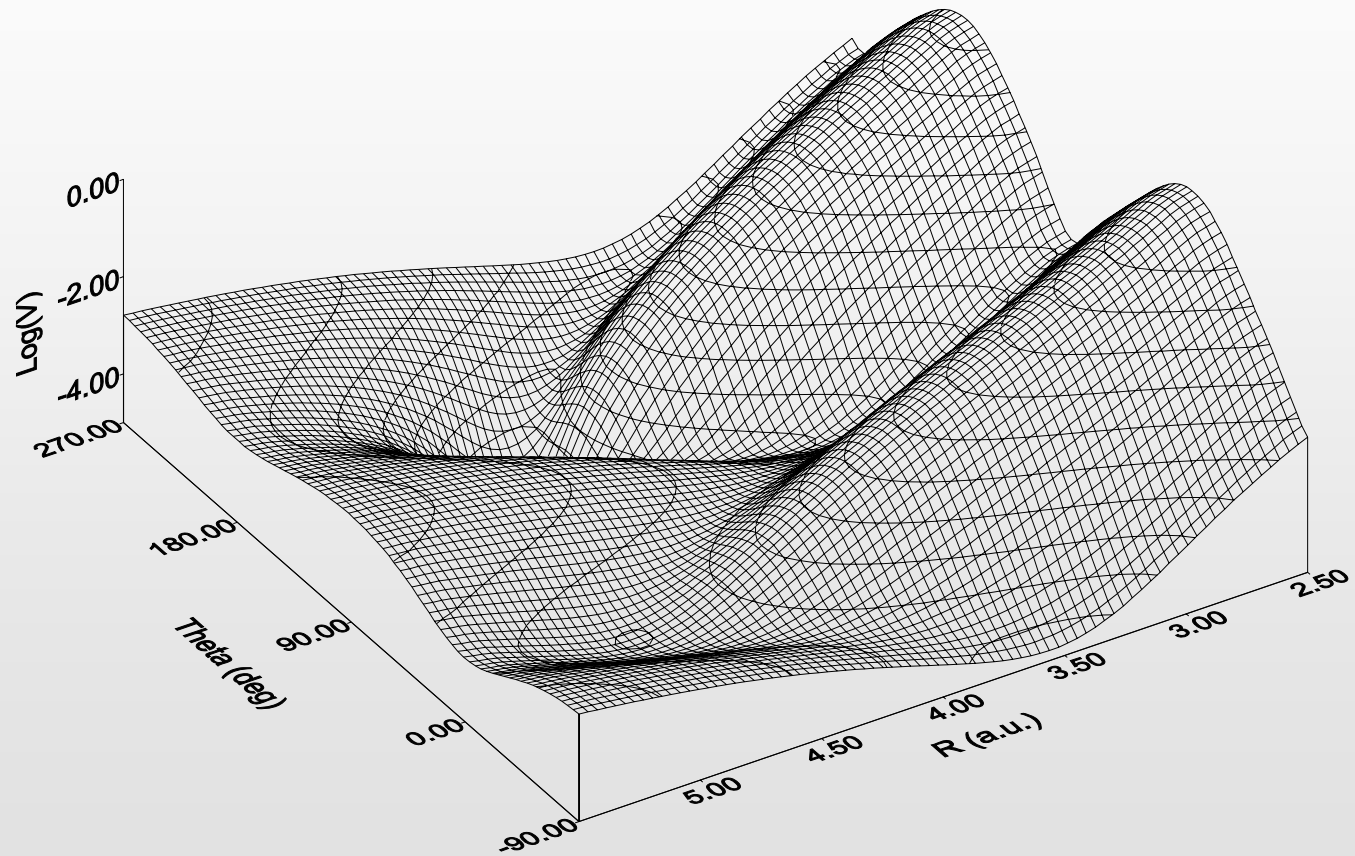
# HO<sub>2</sub>



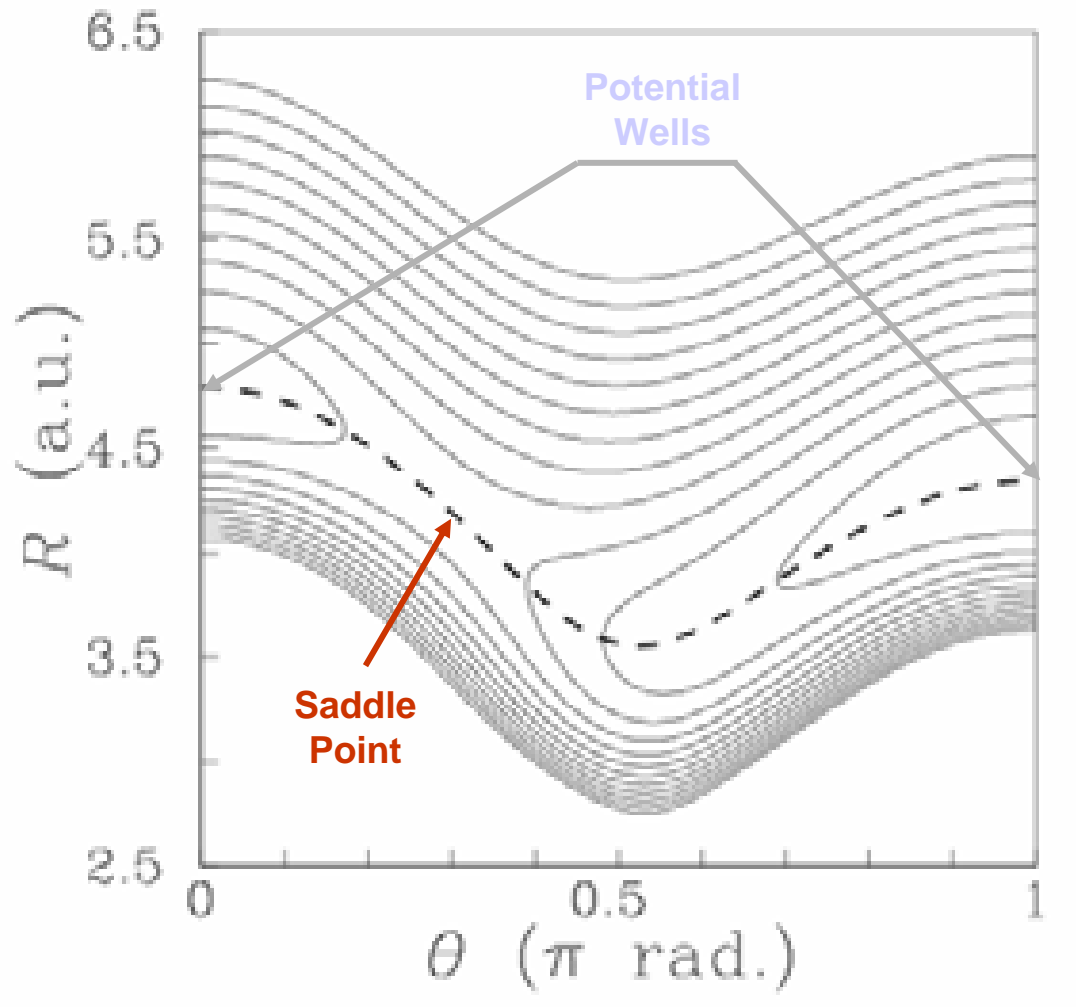
# HCP



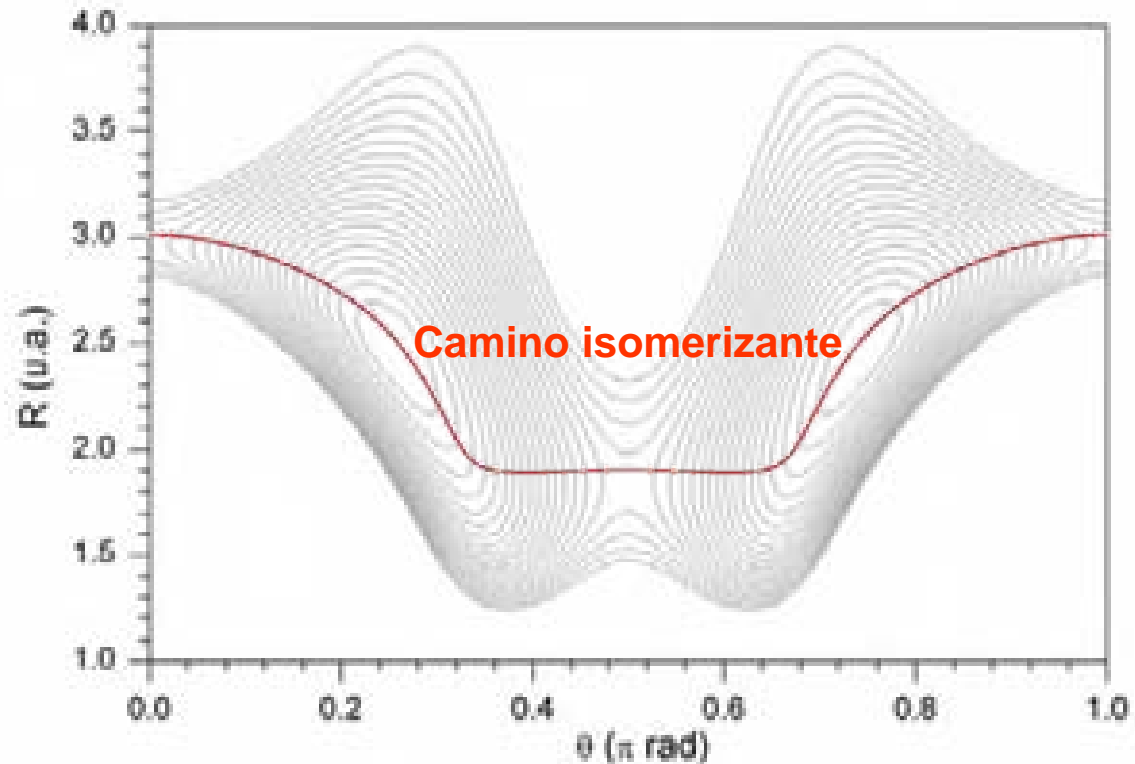
# LiCN



# LiCN

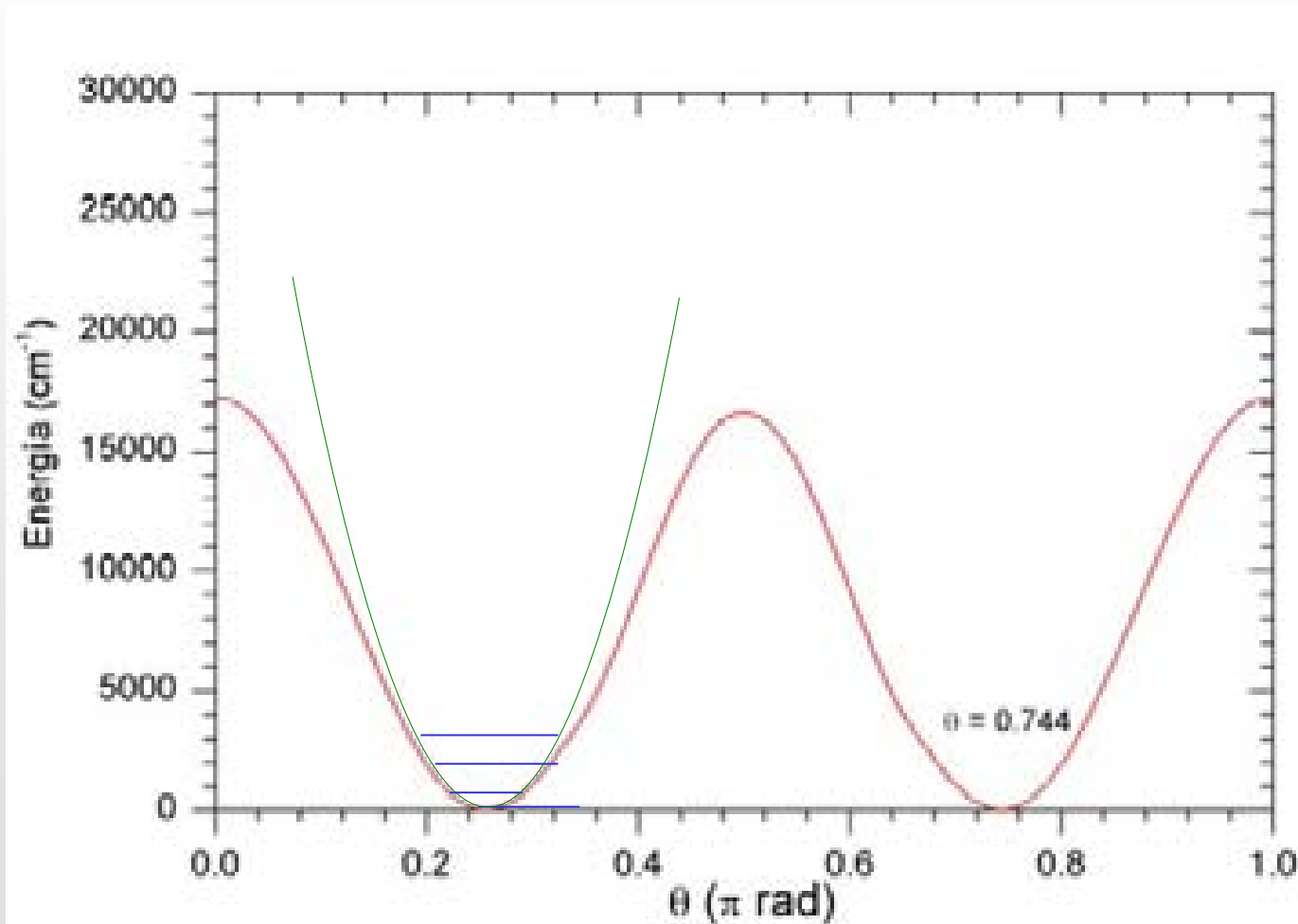


**CALCULATION METHOD:** Búsqueda iterativa de puntos tal que, partiendo de un extremo, la ganancia o pérdida de energía sea mínima.

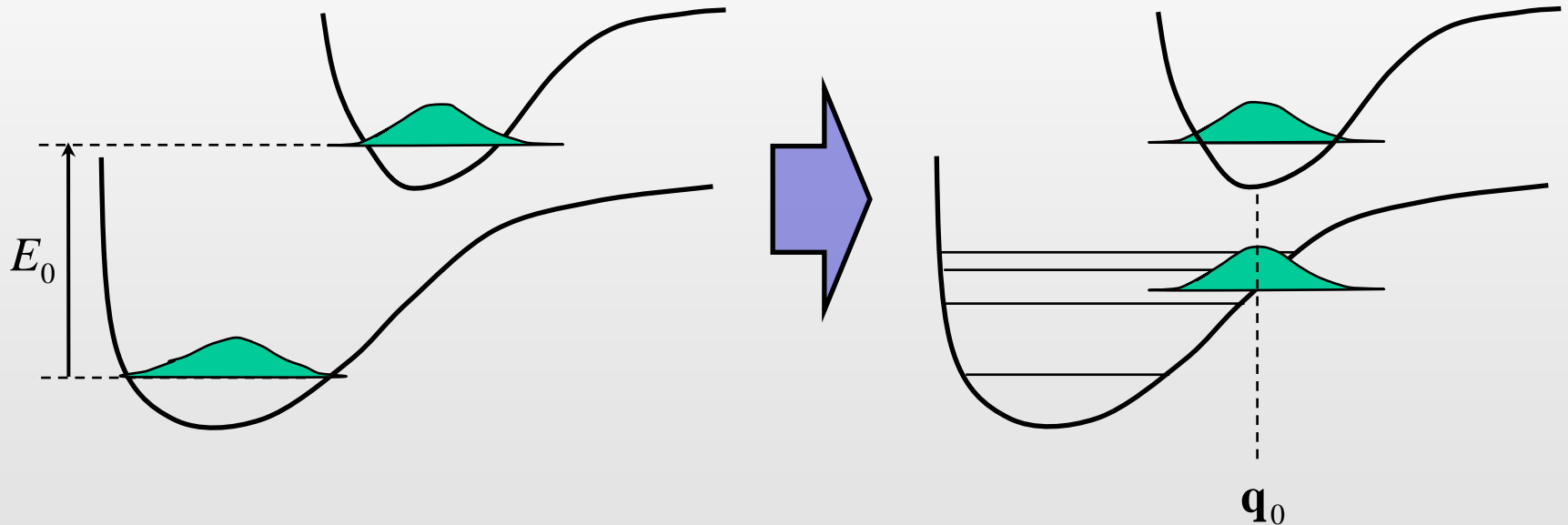


**Fitting to Fourier Series**

$$R_{MEP-i}(\theta) = C_0^{MEP-i} + \sum_{k=1}^9 C_k^{MEP-i} \cos(2k\theta) \quad R_{MEP-ni}(\theta) = C_0^{MEP-ni} + \sum_{k=1}^{14} C_k^{MEP-ni} \cos(2k\theta)$$



- **Espectroscopía por bombeo de emisión estimulada**



**Láser de frecuencia fija  
(bombeo)**

**Láser de frecuencia variable  
(emisión estimulada)**



## INTERÉS:

Procesos de Transferencia de Energía

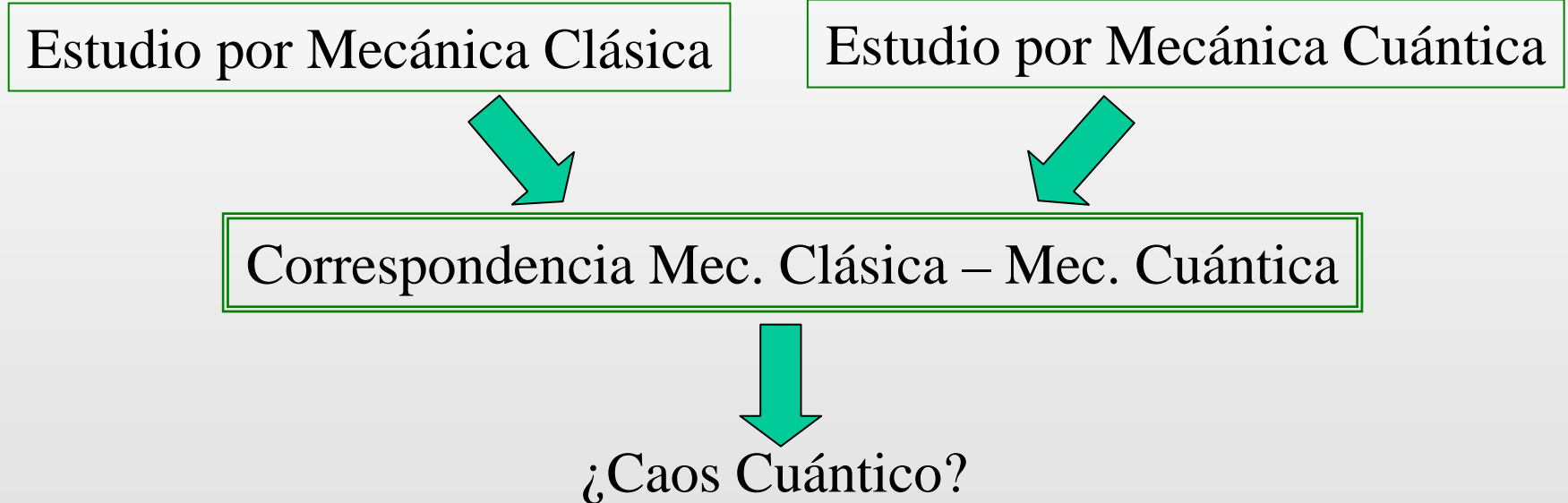


Puede dar lugar a Reacciones Químicas

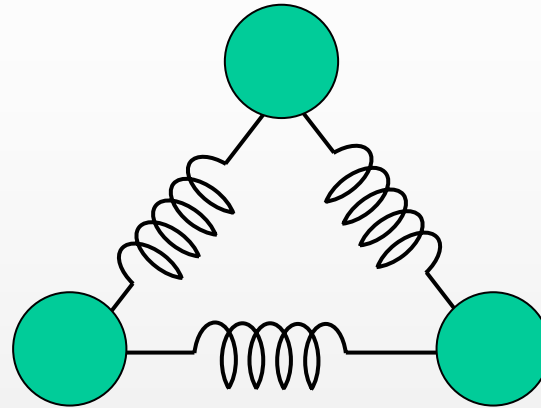


Química Selectiva con Láser

## OBJETIVO DE NUESTRO ESTUDIO



## MANIFESTACIONES CUÁNTICAS DEL CAOS



MOLECULA = Suma de Osciladores

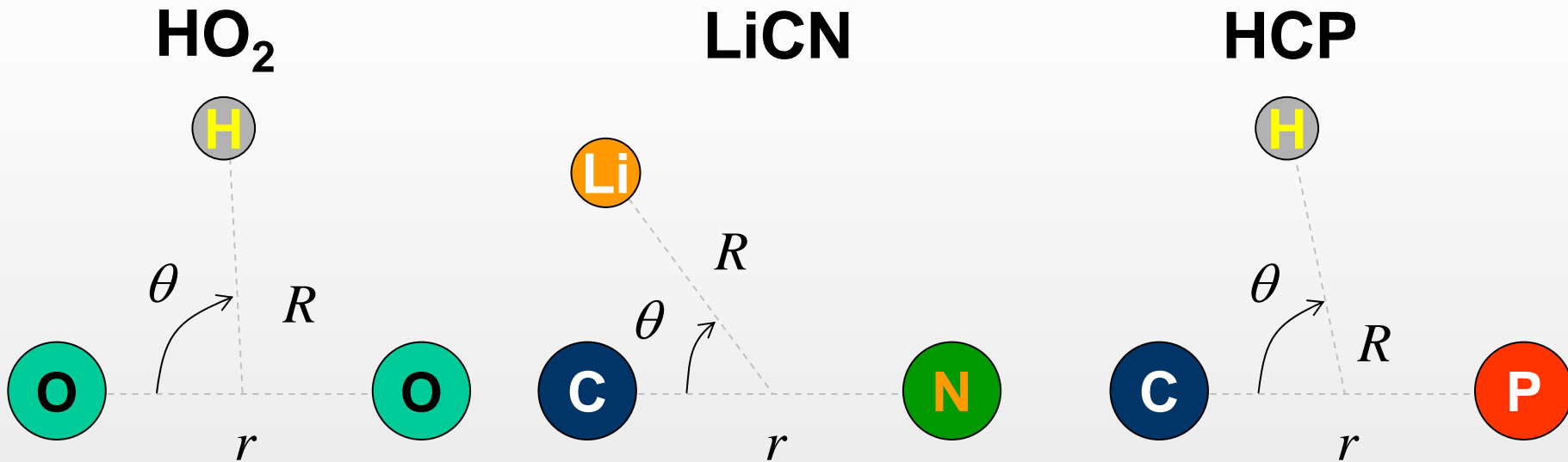
## SISTEMAS HAMILTONIANOS

Formados por un conjunto de osciladores acoplados



## SISTEMAS NO LINEALES

# SISTEMA MOLECULAR



$$H(R, r, \theta, P_R, P_r, P_\theta) = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left[ \frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2} \right] \frac{P_\theta^2}{2} + V(R, r, \theta) = E$$

## Ecuaciones del Movimiento de Hamilton (2 grados de libertad)

$$H(R, \theta, P_R, P_\theta) = \frac{P_R^2}{2\mu_1} + \left[ \frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r_e^2} \right] \frac{P_\theta^2}{2} + V(R, \theta) = E$$

$$\dot{q}_i = \frac{\partial H(\vec{q}, \vec{p}, t)}{\partial p_i} \quad q_1 \equiv R \quad q_2 \equiv \theta$$

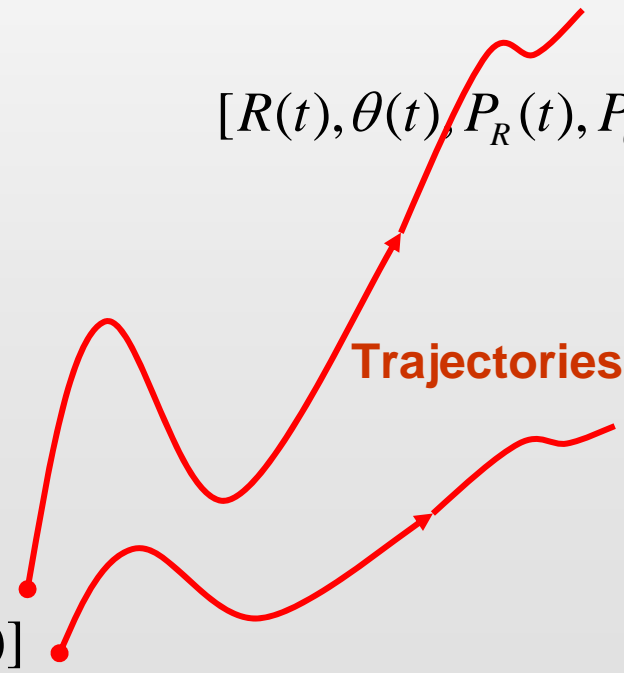
$$\dot{p}_i = -\frac{\partial H(\vec{q}, \vec{p}, t)}{\partial q_i} \quad p_1 \equiv P_R \quad p_2 \equiv P_\theta$$

$$[R(t), \theta(t), P_R(t), P_\theta(t)]$$

Trajectories

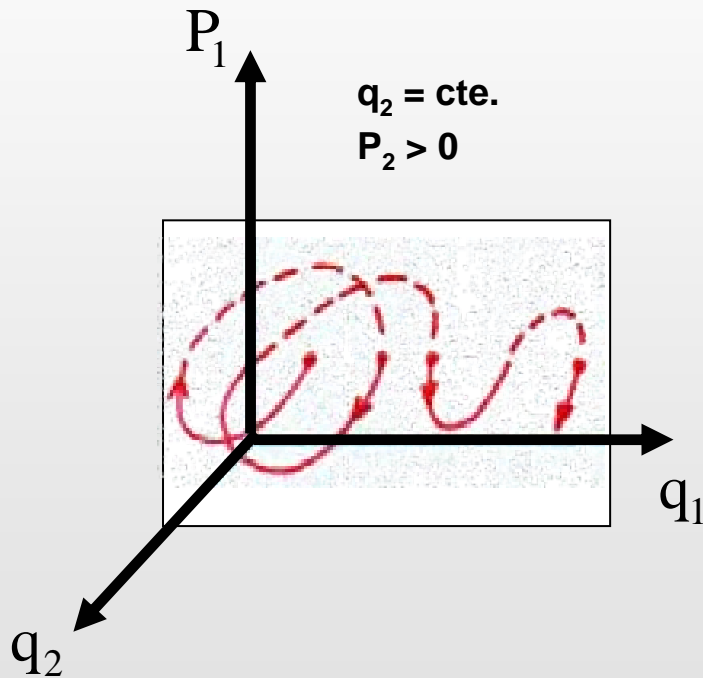
$$[R_1(t_0), \theta_1(t_0), P_{R_1}(t_0), P_{\theta_1}(t_0)]$$

$$[R_2(t_0), \theta_2(t_0), P_{R_2}(t_0), P_{\theta_2}(t_0)]$$

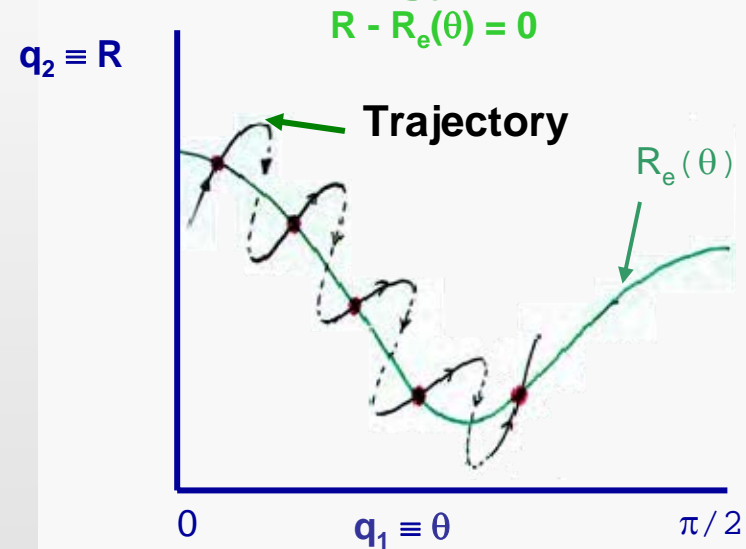


# MECÁNICA CLÁSICA

## Superficie de Sección de Poincaré



### Surface of Section: **Minimum Energy Path**



# MECÁNICA CLÁSICA

Action- Angles variables Representation:

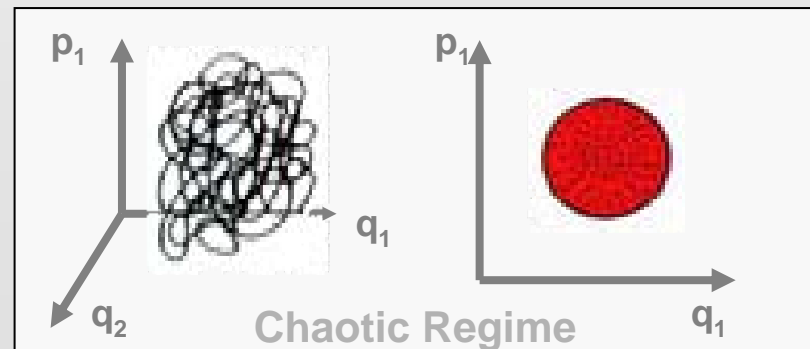
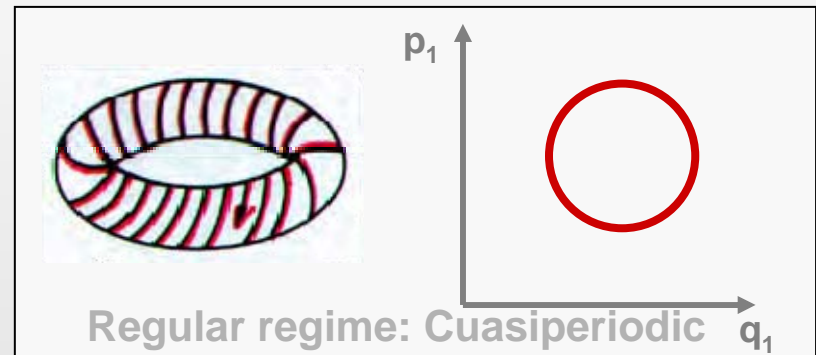
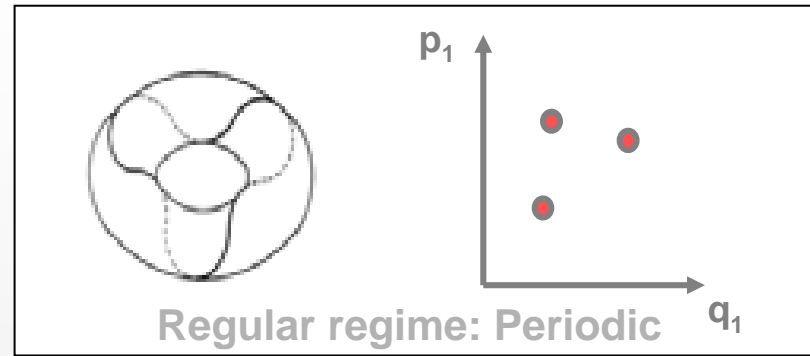
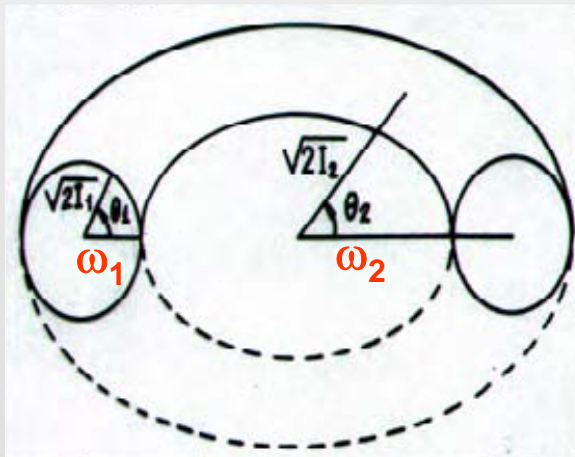
$$(\vec{q}, \vec{p}) \xrightarrow{T} (\vec{I}, \vec{\theta})$$

$$H = H(\vec{q}, \vec{p}) \quad H = H(\vec{I})$$

**2 Degrees of freedom: (R,  $\theta$ )**

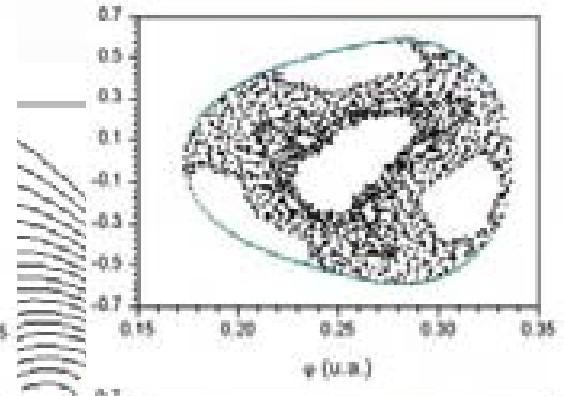
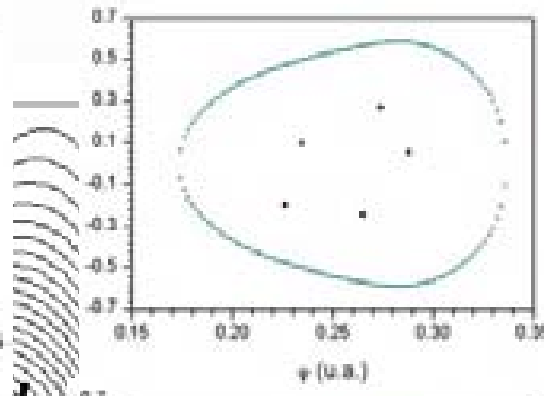
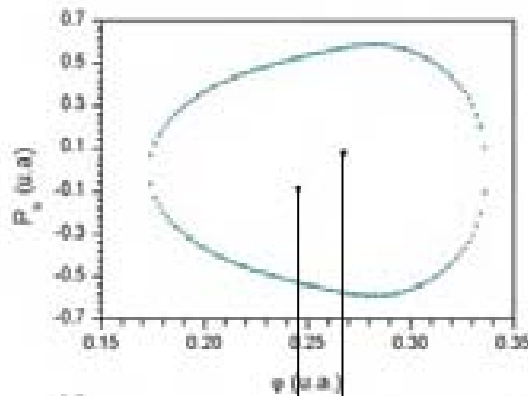


**Trajectories confined in 2D Tori**

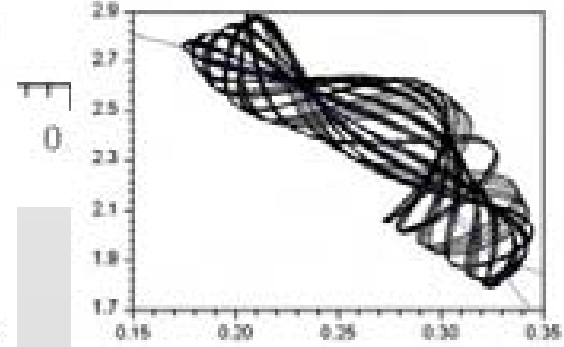
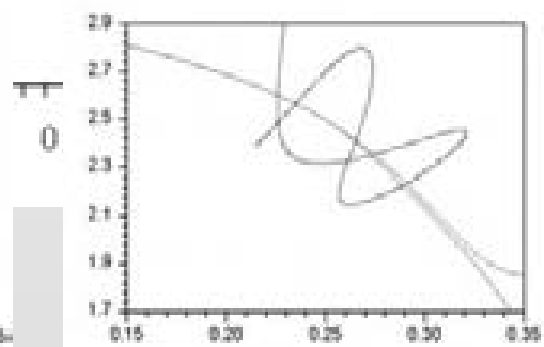
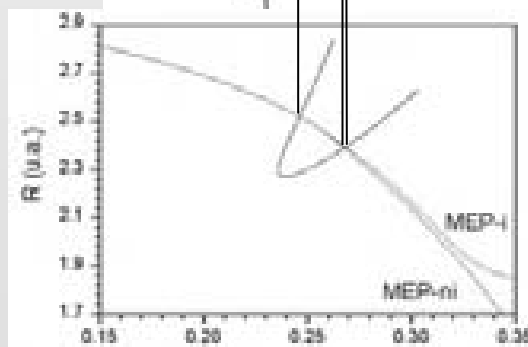
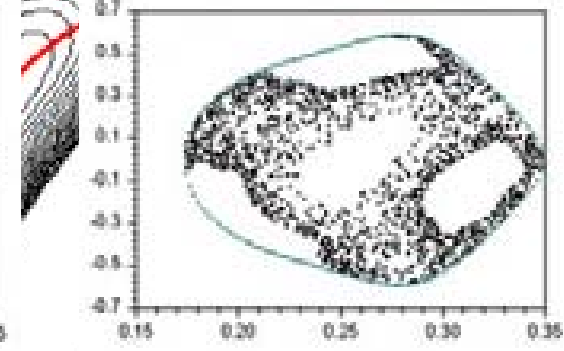
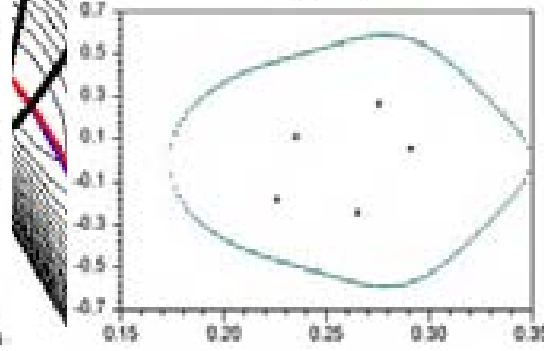
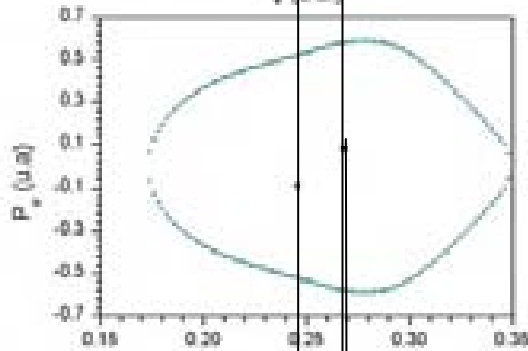


# HO<sub>2</sub>

MEP-ni



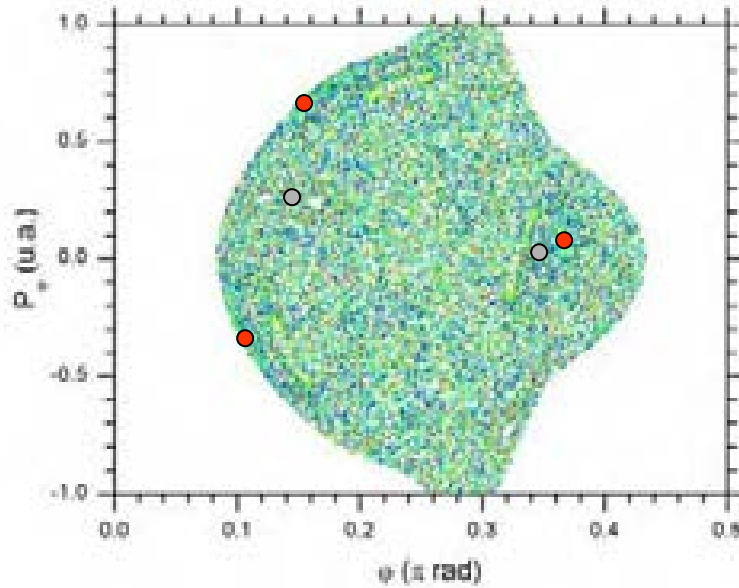
MEP-i





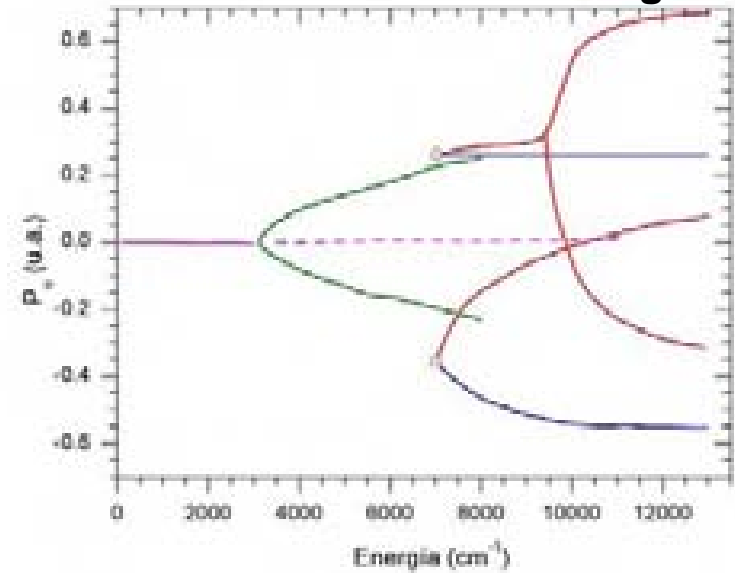
# HO<sub>2</sub>

Superficie de Sección de Poincaré  
 Compuesta

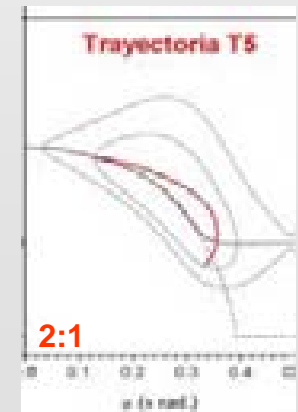
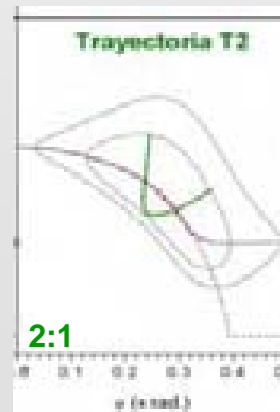
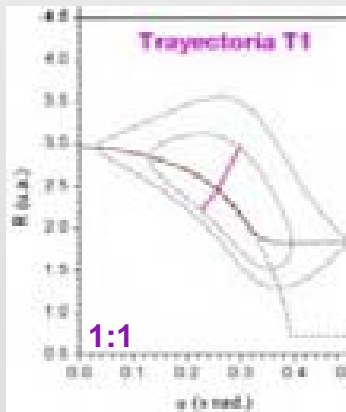


13.000 cm<sup>-1</sup>

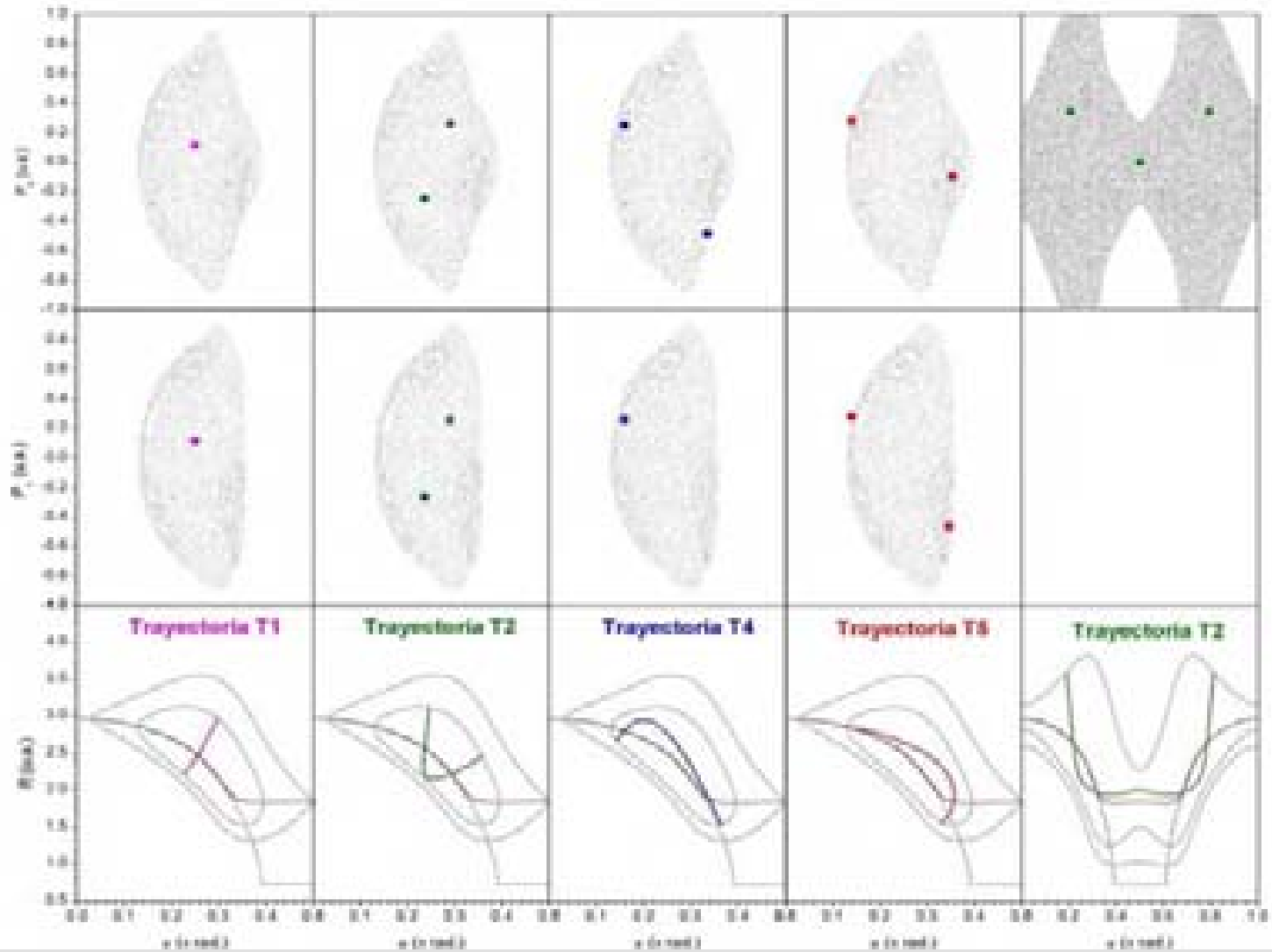
Bifurcation Diagram

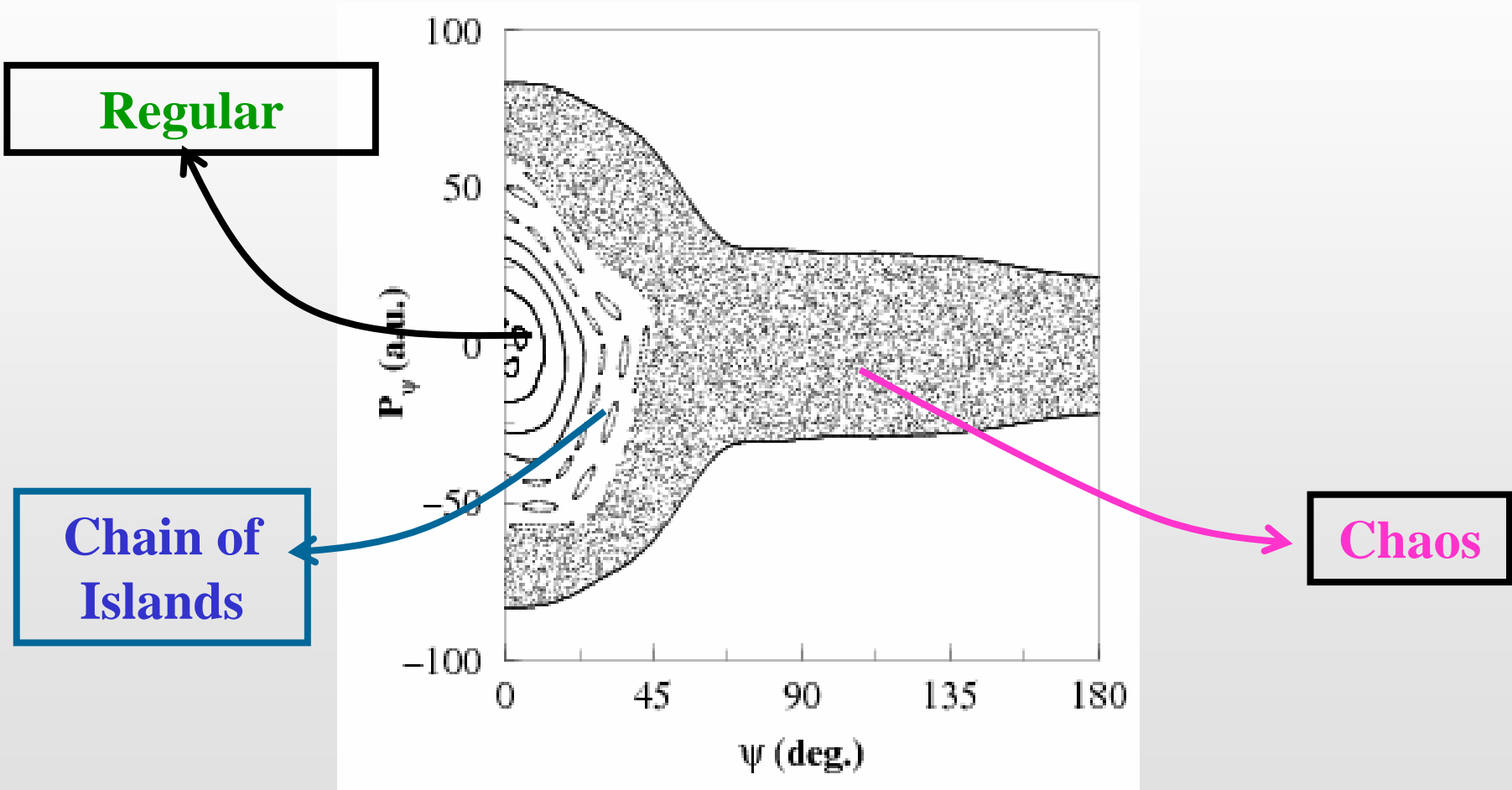


Familias de  
 Órbitas periódicas



# HO<sub>2</sub>

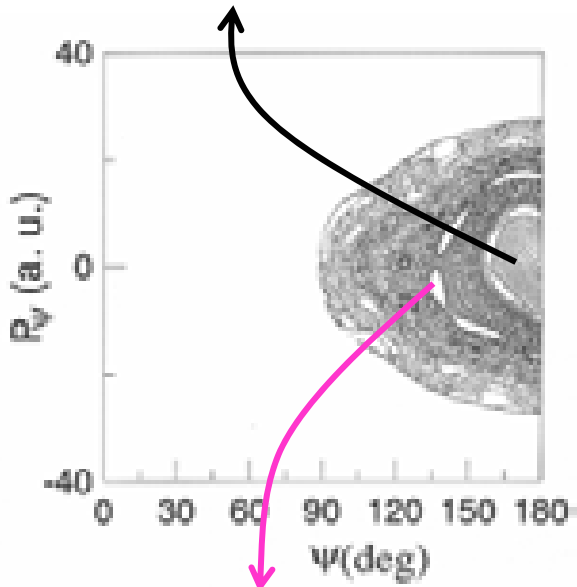




# LiCN

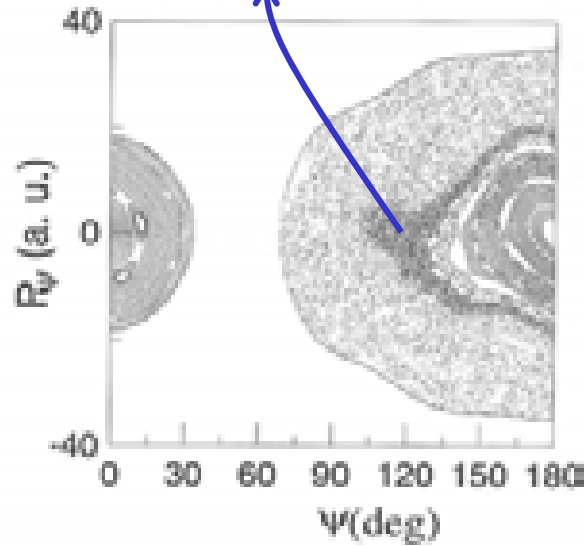


**Regularidad (toros)**

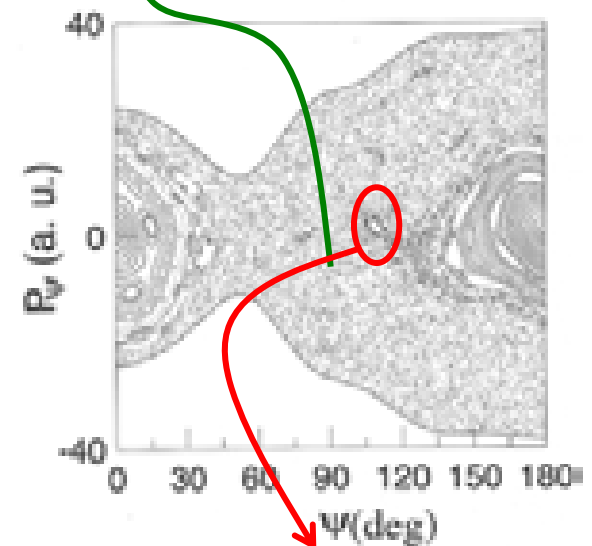


**Cadenas de islas**

**Cantoro**

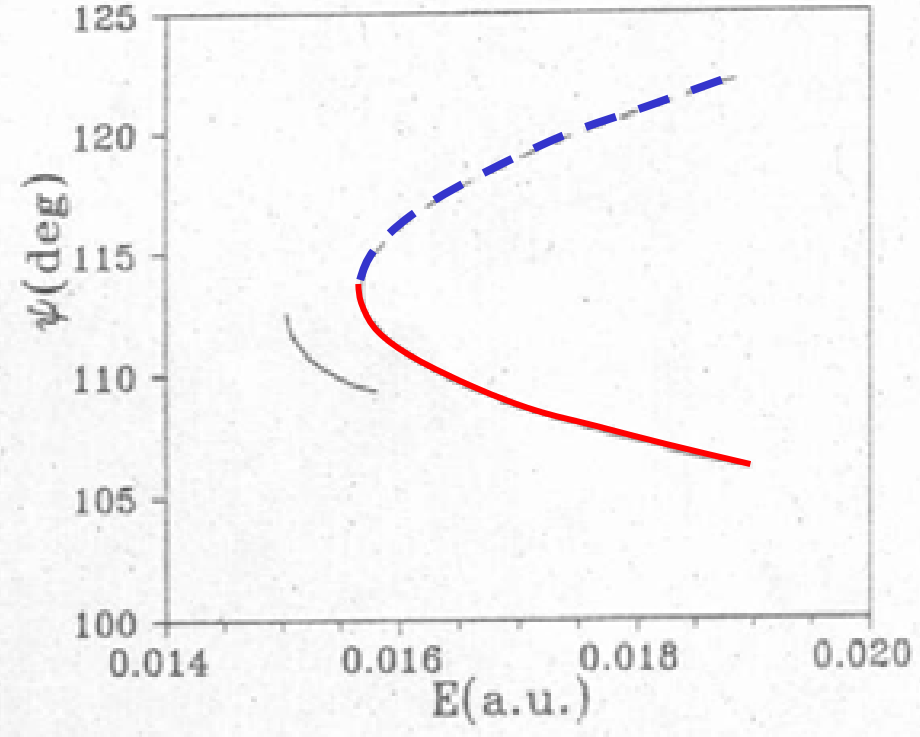
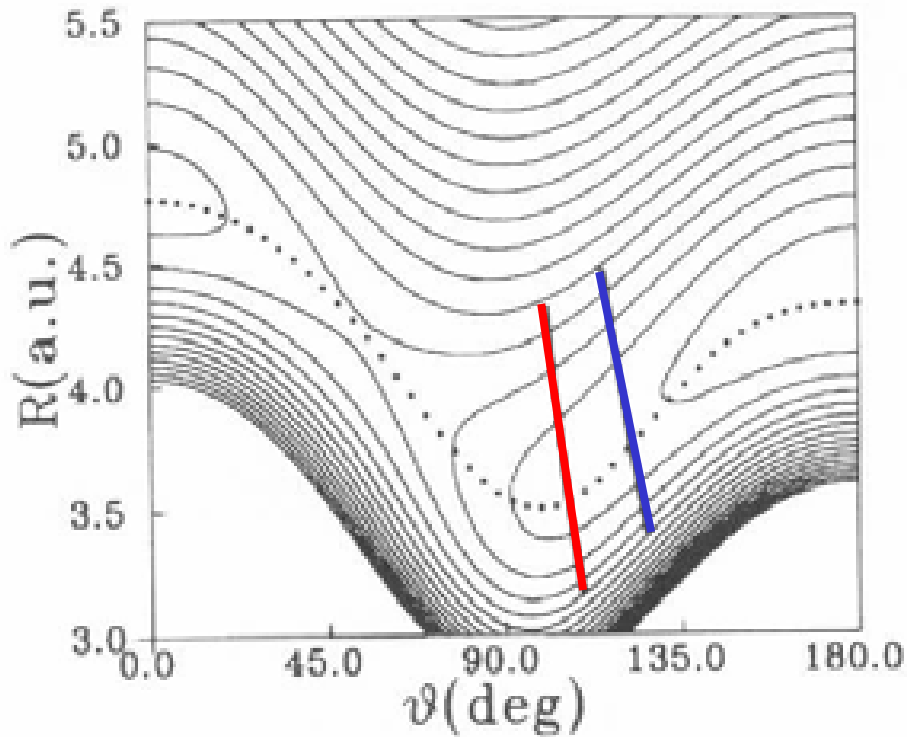


**CAOS (ergodicidad)**

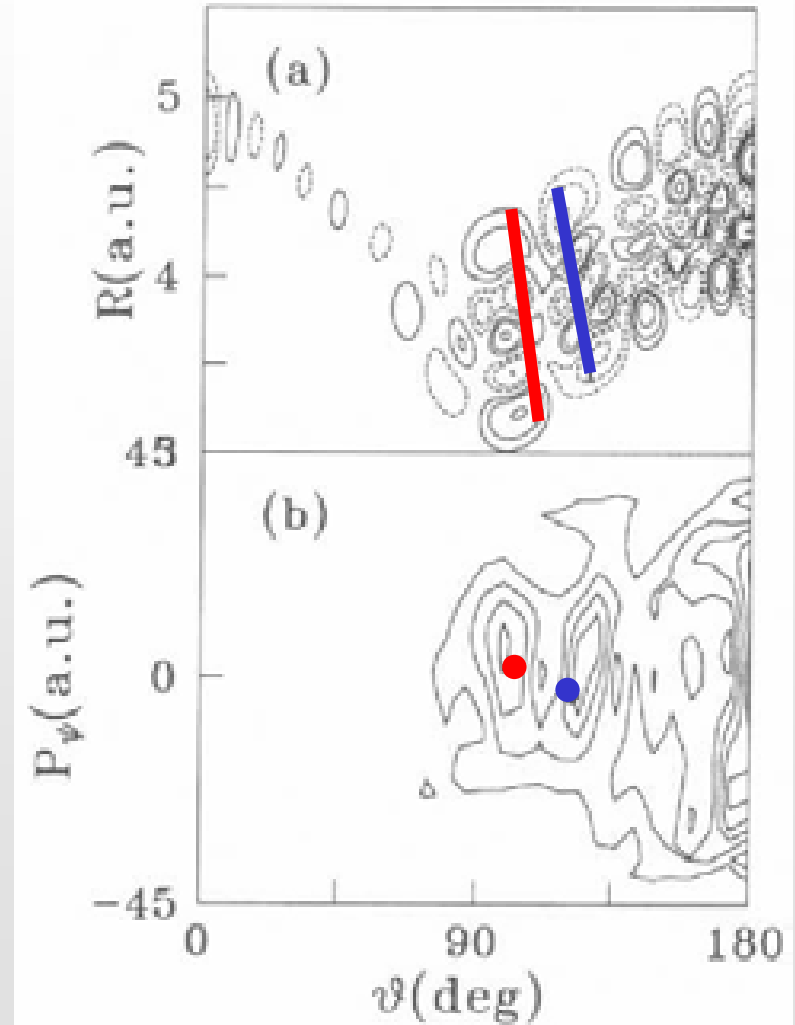
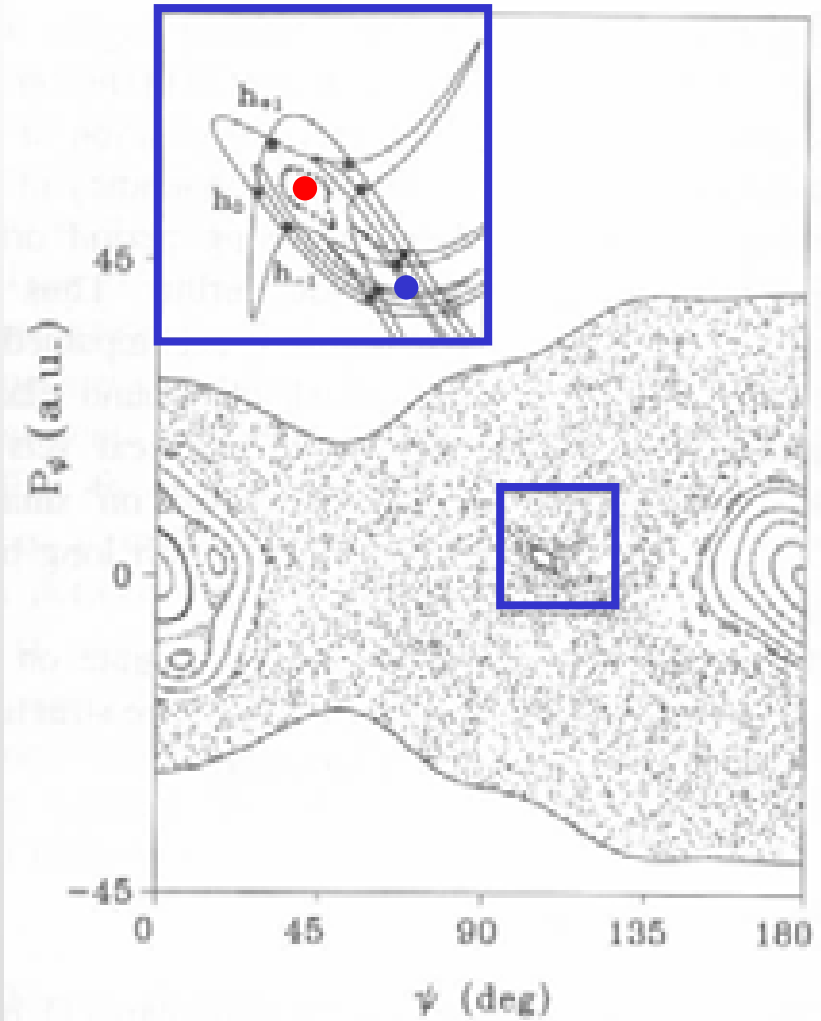


**Bifurcación silla-nodo**

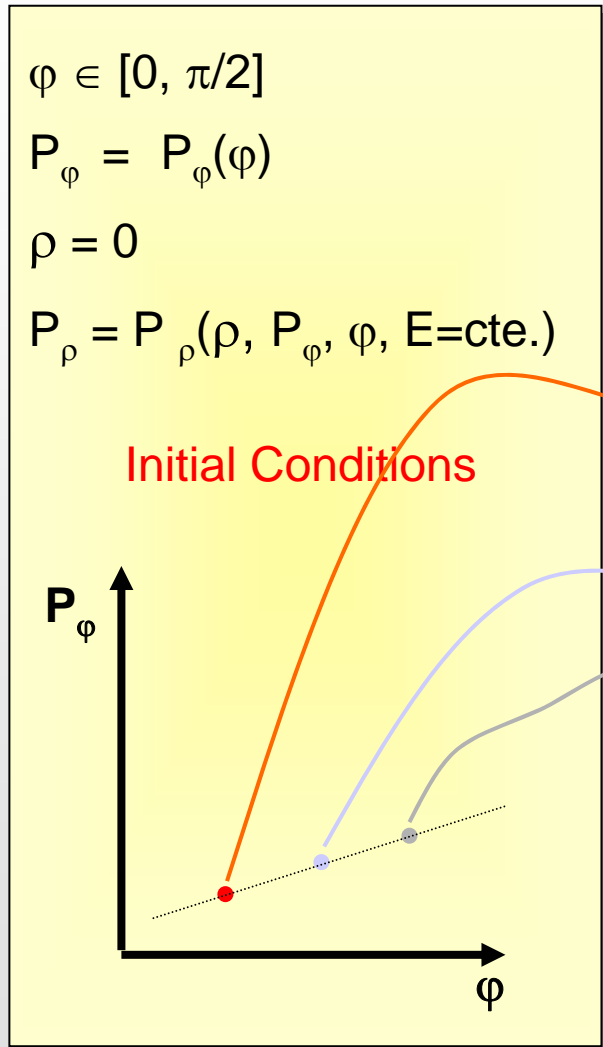
# Bifurcación Silla-Nodo



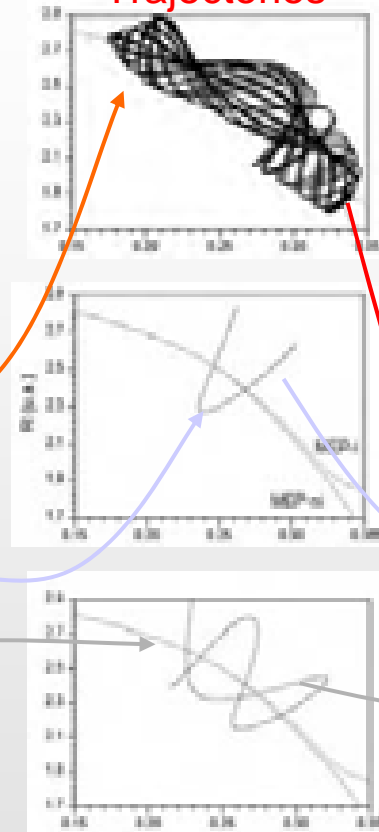
# Bifurcación Silla-Nodo



# MAPA DE FRECUENCIAS



**Trajectories**

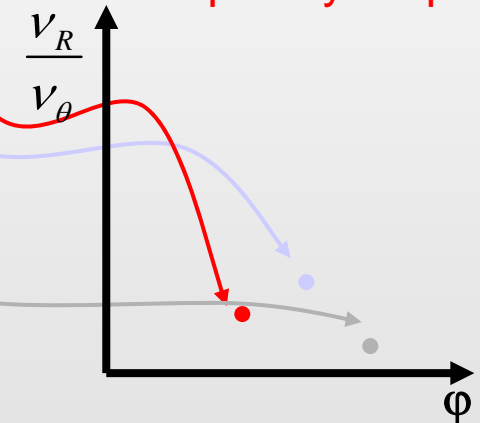


## Frequency Analysis

$$f_R = R + iP_R \rightarrow (v_R, v_\theta)$$

$$f_\theta = \theta + iP_\theta$$

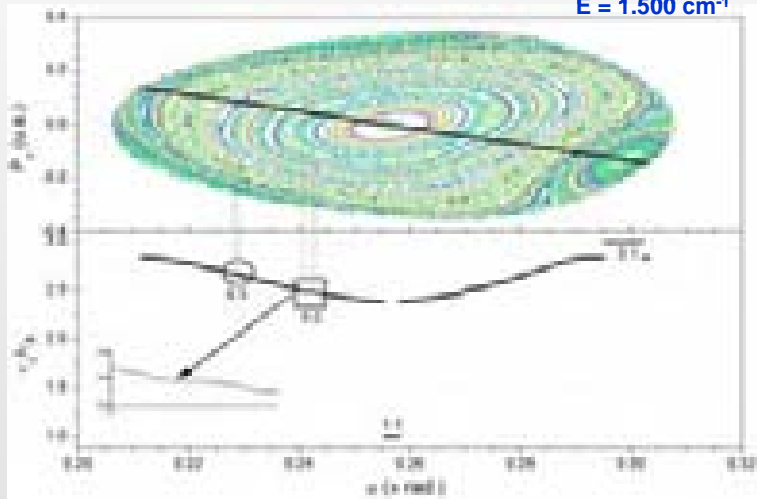
**Frequency Map**



# ANÁLISIS DE FRECUENCIAS

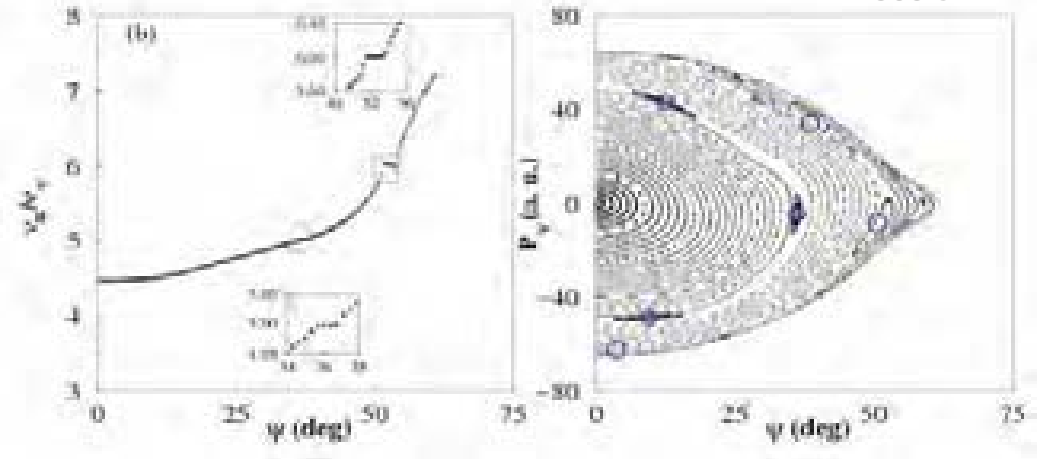
**HO<sub>2</sub>**

$E = 1.500 \text{ cm}^{-1}$



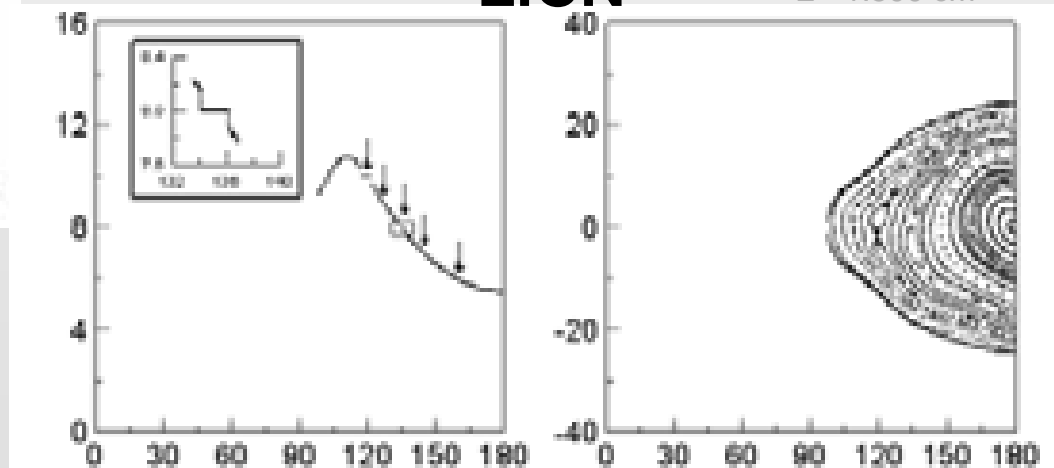
**HCP**

$E = 17.500 \text{ cm}^{-1}$



**LiCN**

$E = 1.500 \text{ cm}^{-1}$

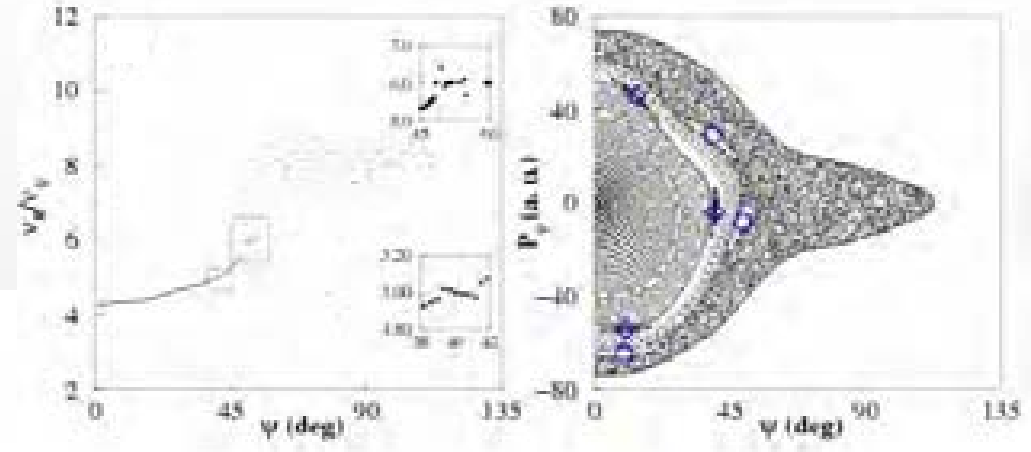




# ANÁLISIS DE FRECUENCIAS

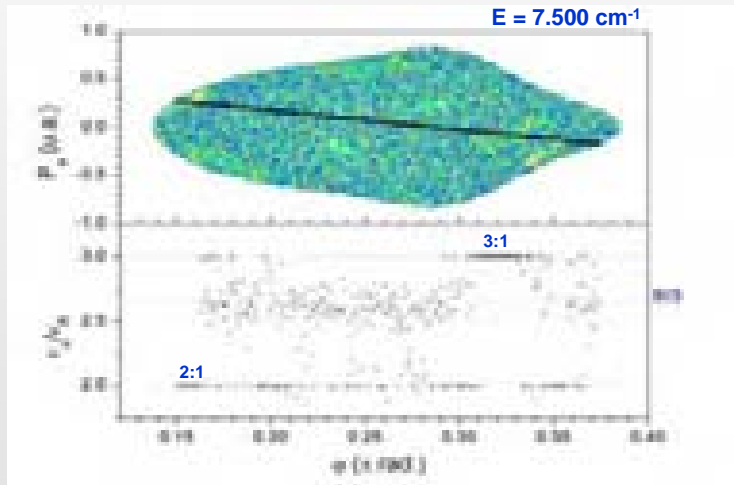
## HCP

$E = 23.000 \text{ cm}^{-1}$



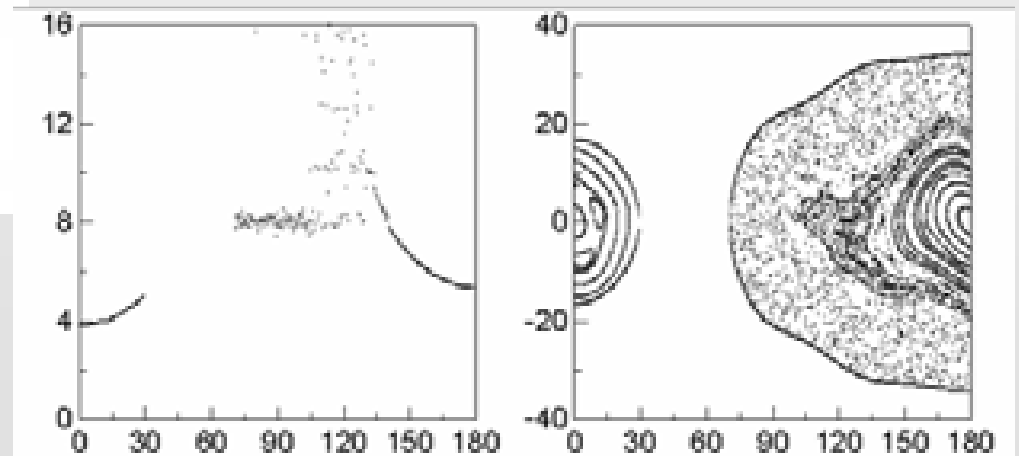
## HO<sub>2</sub>

$E = 7.500 \text{ cm}^{-1}$



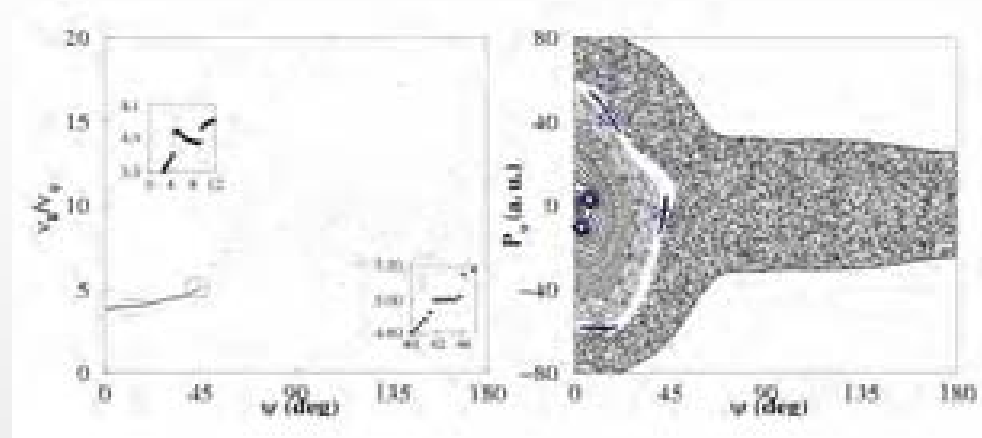
## LiCN

$E = 2.950 \text{ cm}^{-1}$



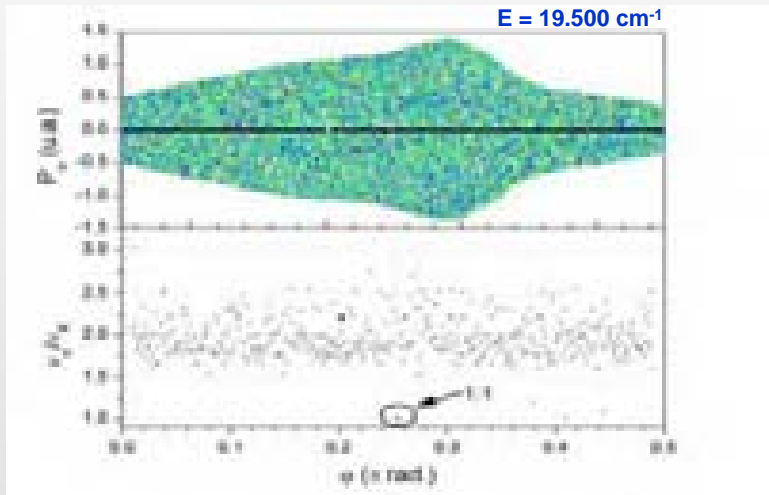
## HCP

$E = 30.000 \text{ cm}^{-1}$



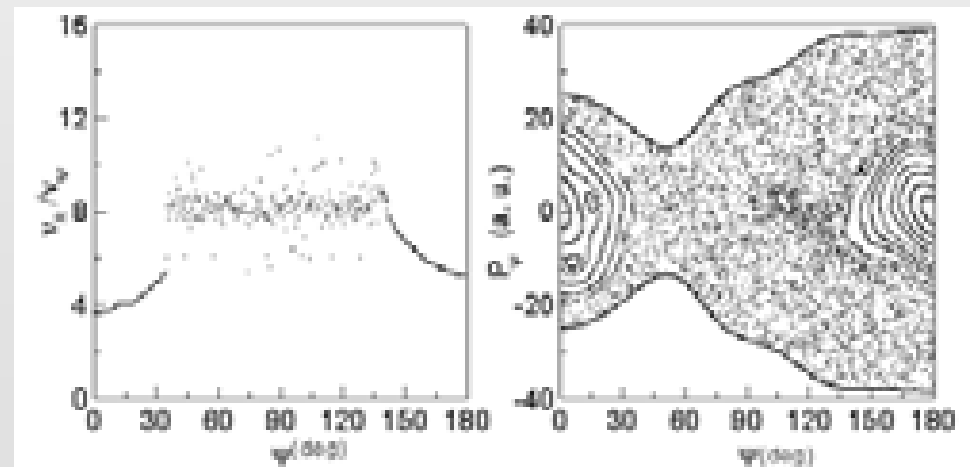
## HO<sub>2</sub>

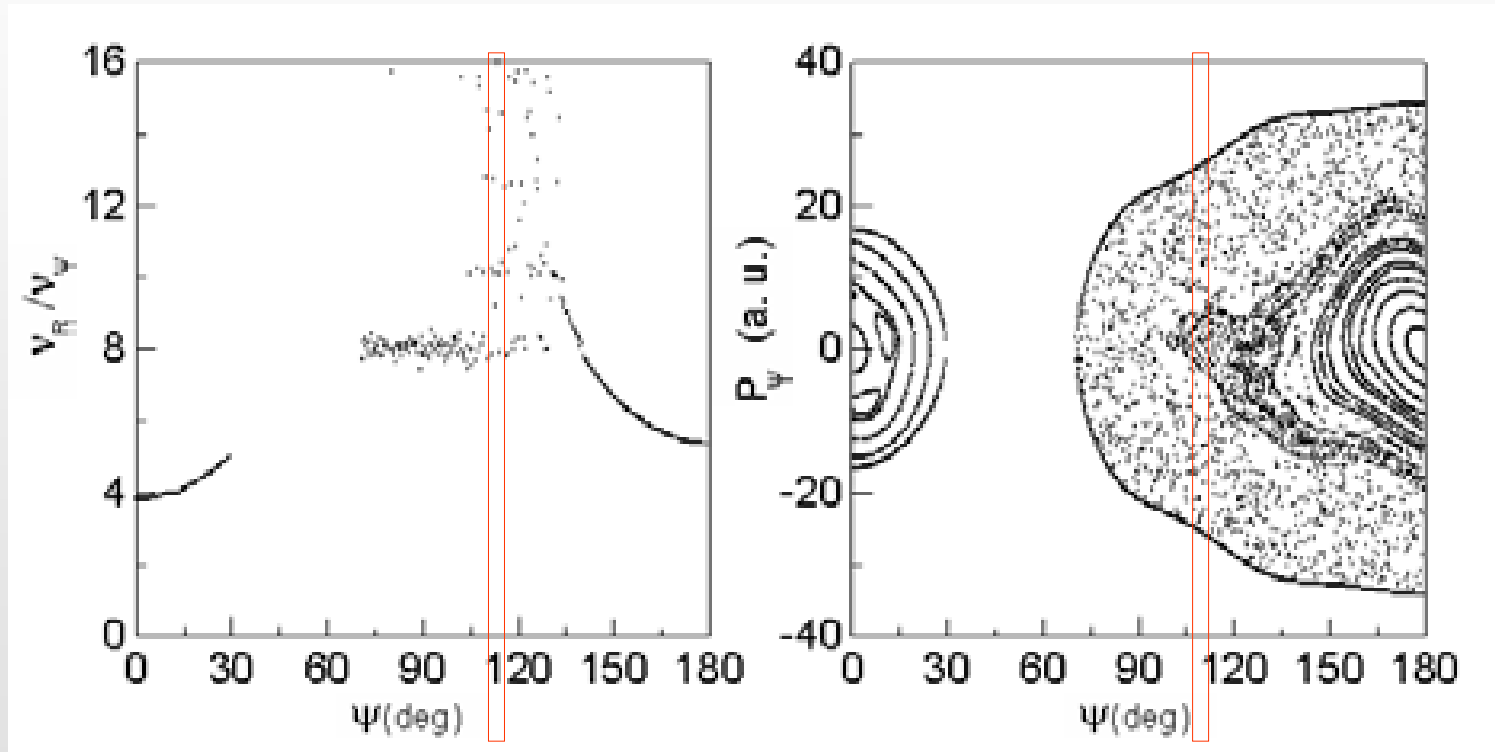
$E = 19.500 \text{ cm}^{-1}$

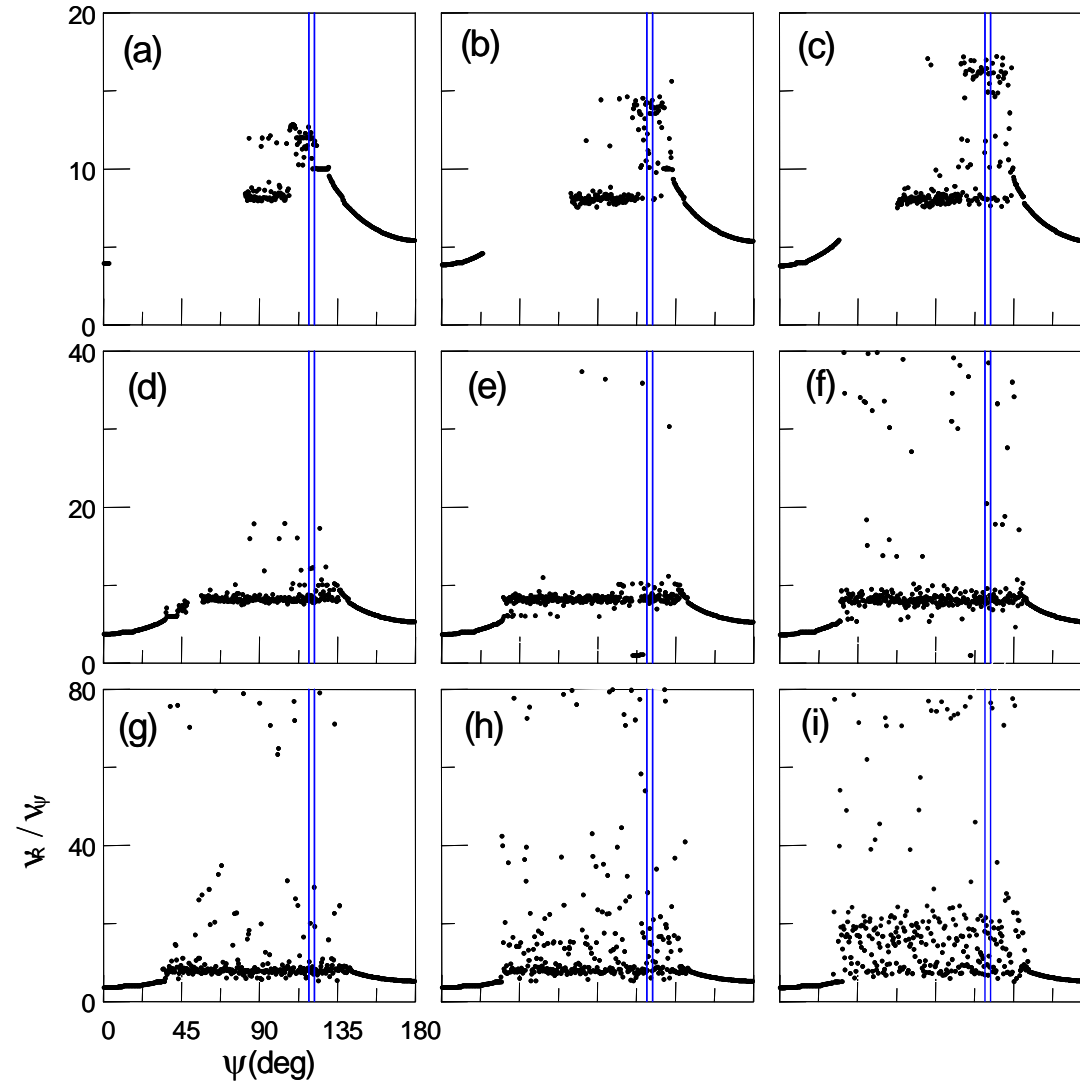


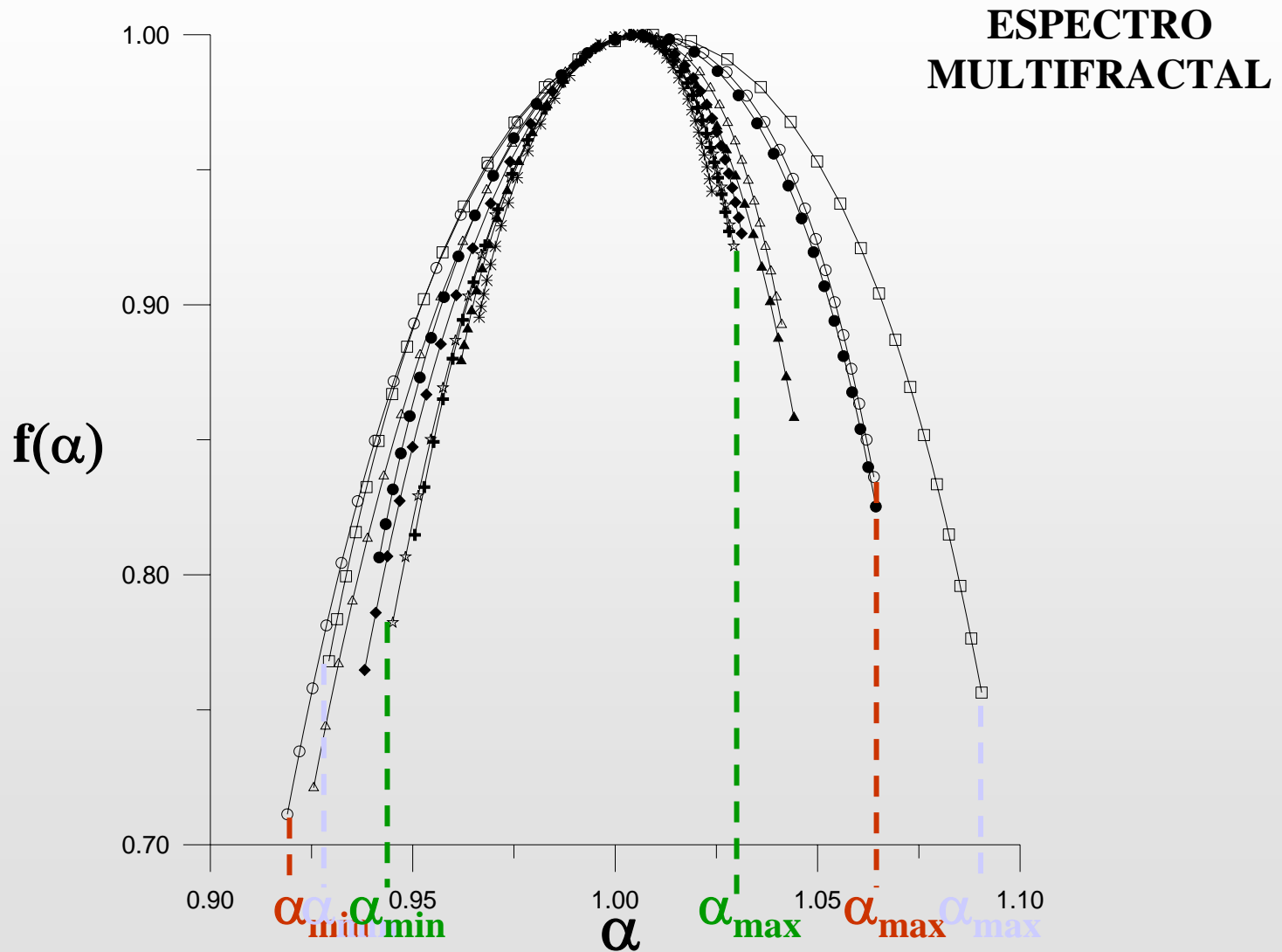
## LiCN

$E = 3.800 \text{ cm}^{-1}$

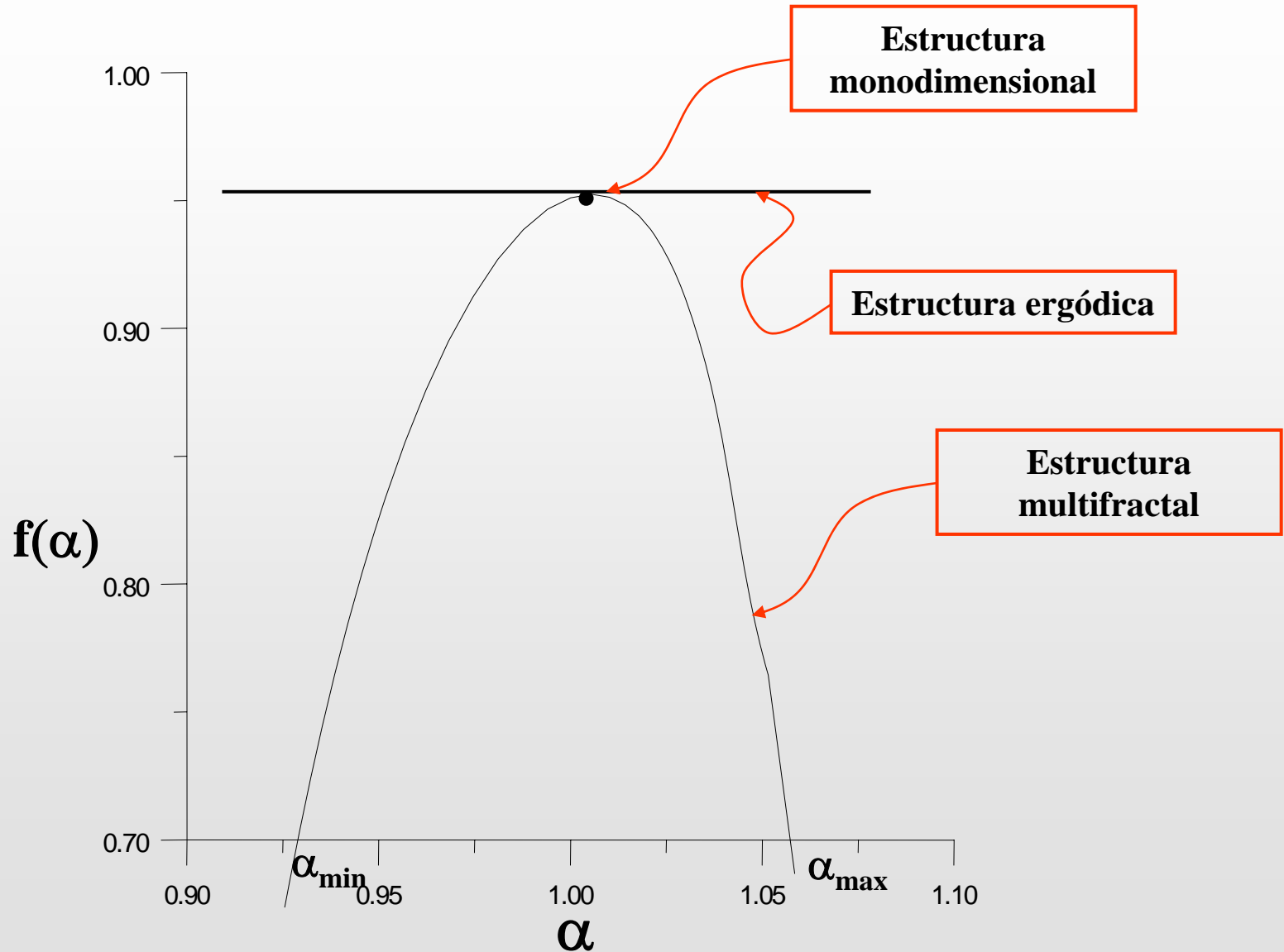


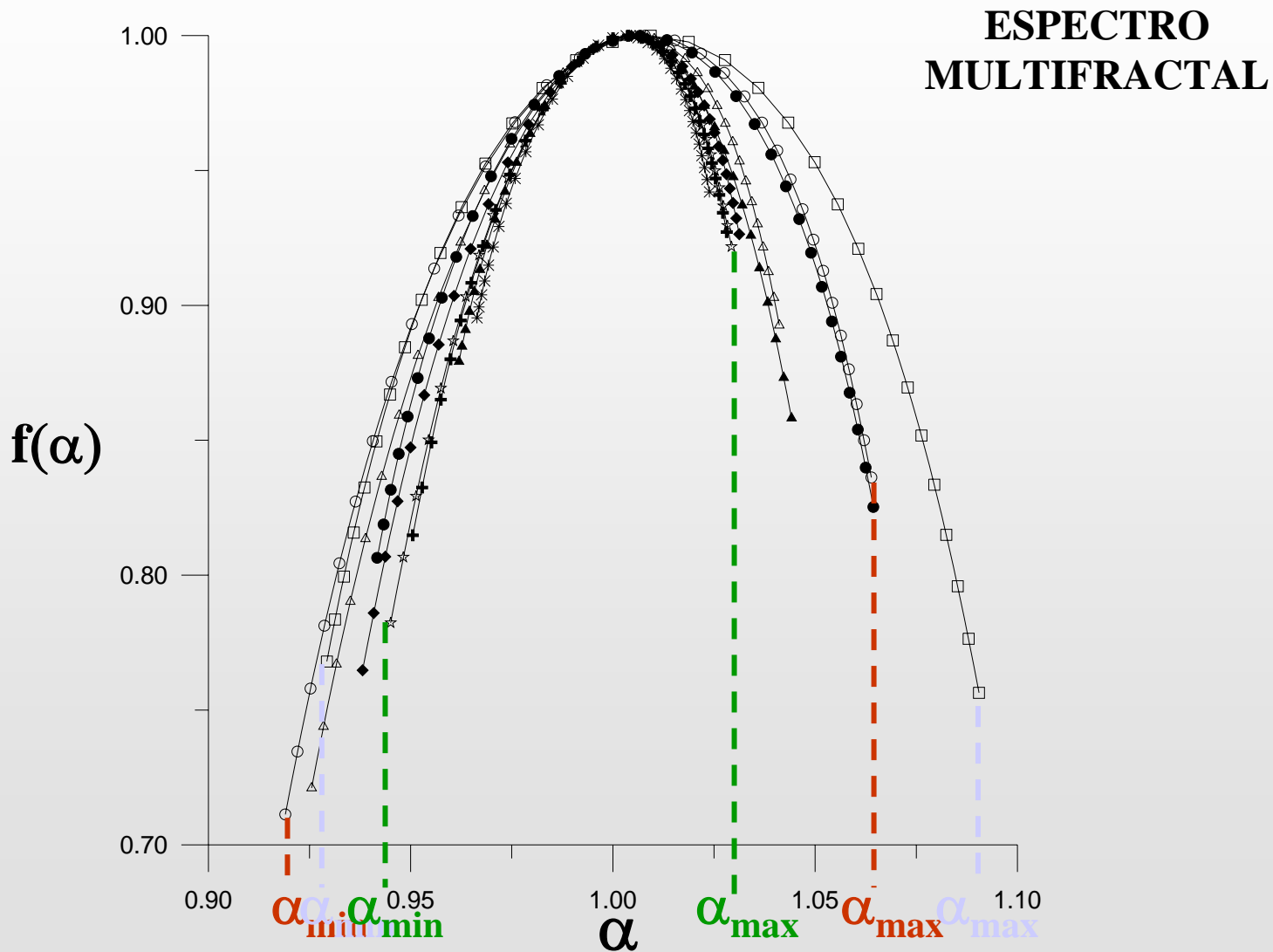






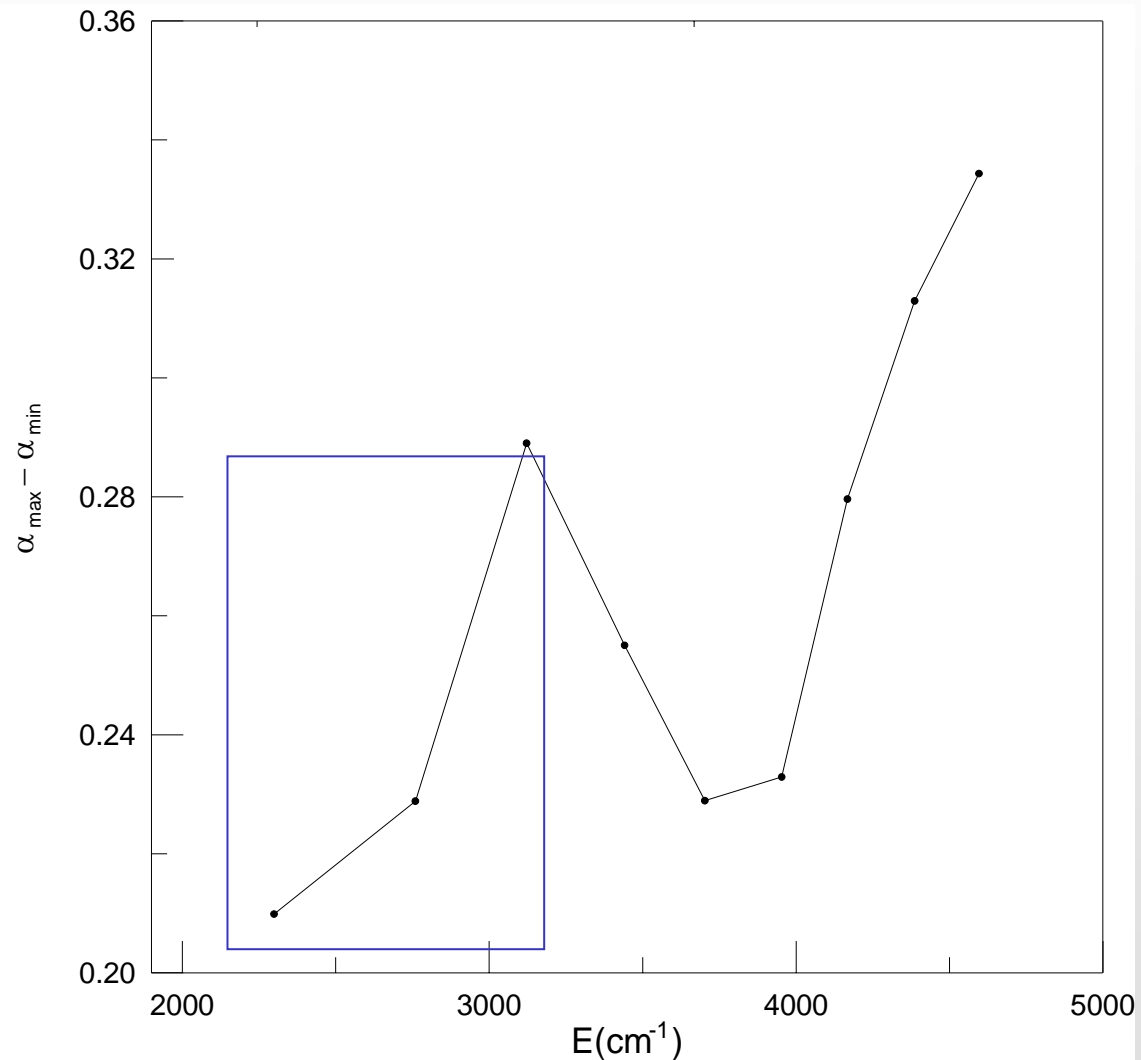
# ANÁLISIS MULTIFRACTAL





# ANÁLISIS MULTIFRACTAL

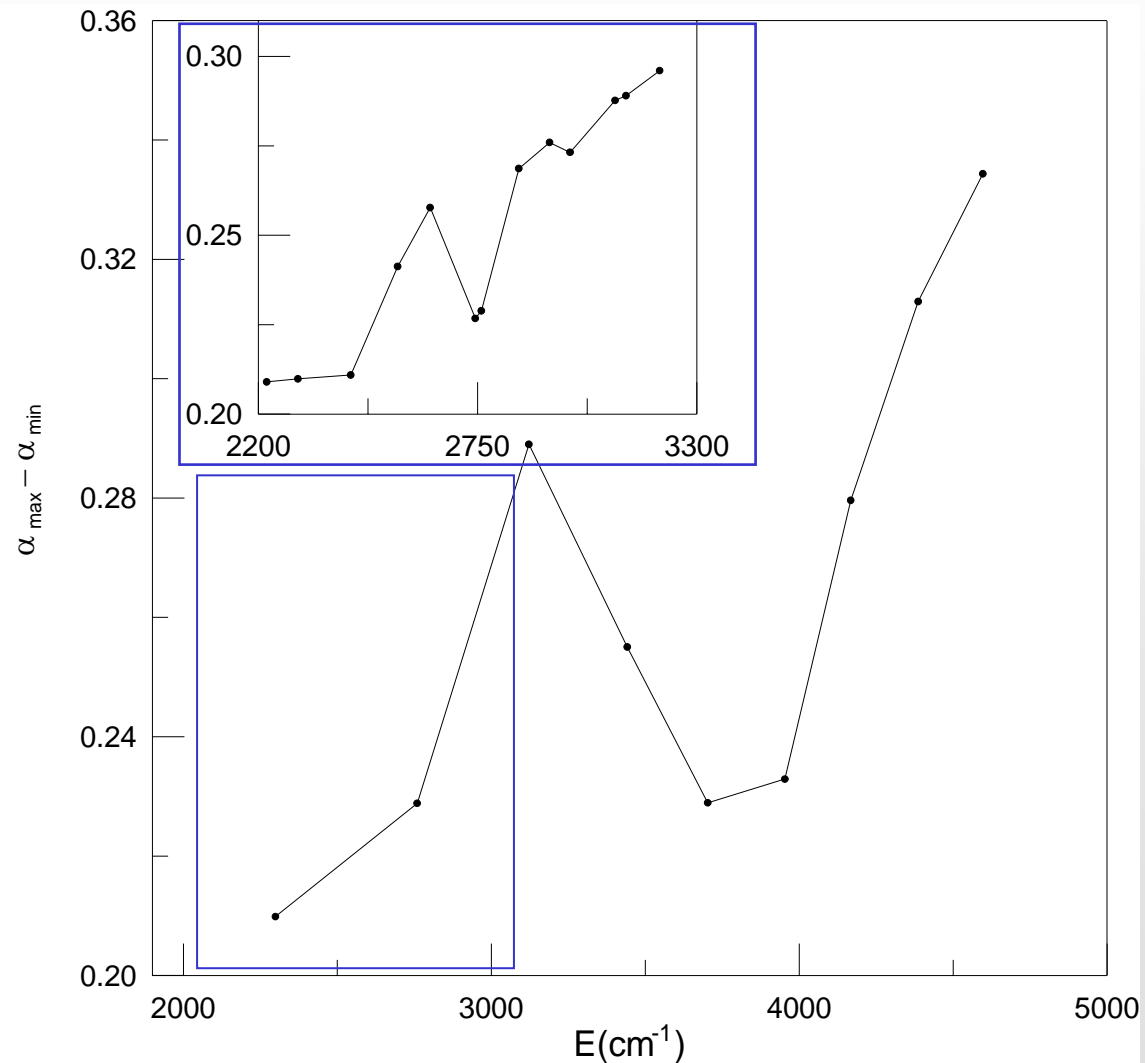
$\alpha_{max} - \alpha_{min}$  vs ENERGÍA





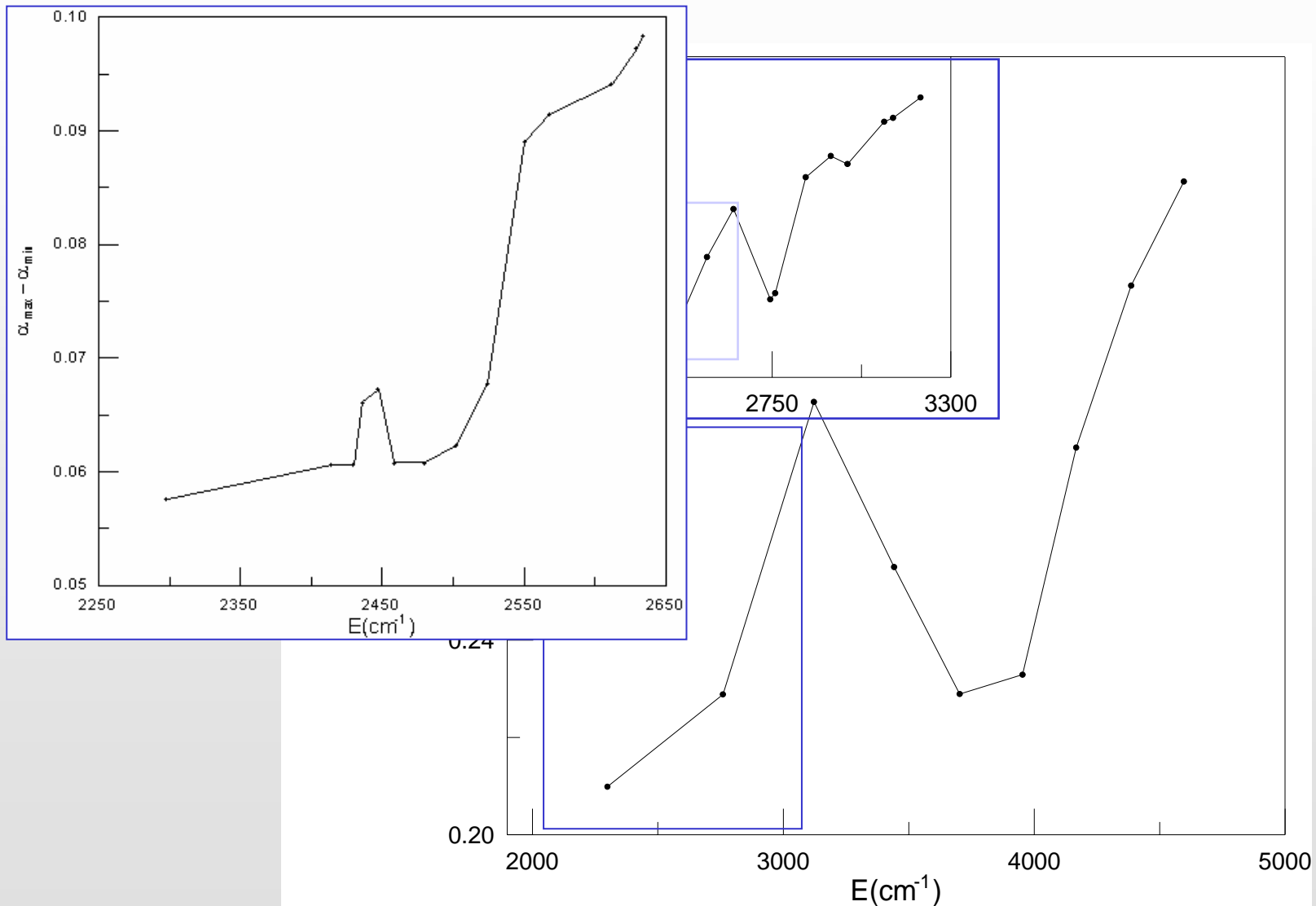
# ANÁLISIS MULTIFRACTAL

$\alpha_{max} - \alpha_{min}$  vs ENERGÍA

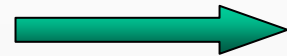


# ANÁLISIS MULTIFRACTAL

$\alpha_{max} - \alpha_{min}$  vs ENERGÍA



• **TOROS KAM**



**BARRERAS TOTALES**

**DESTRUCCIÓN DE TOROS  
ESTRUCTURA MULTIFRACTAL**

• **CANTOROS**  
(Conjuntos de Cantor)  
**FRACTALES**



**BARRERAS PARCIALES**

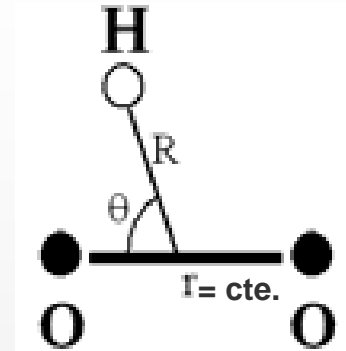
# TRES GRADOS DE LIBERTAD

$$H(R, \theta, P_R, P_\theta) = \frac{P_R^2}{2\mu_1} + \left[ \frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r_{eq.}^2} \right] \frac{P_\theta^2}{2} + V(R, \theta) = E$$



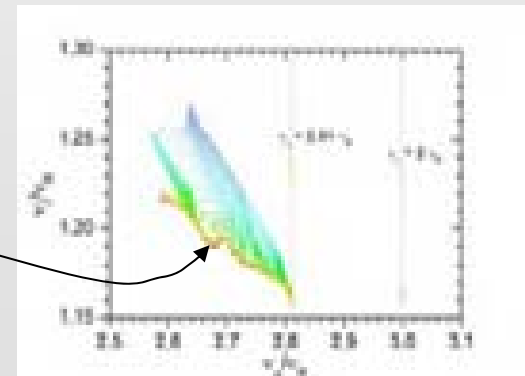
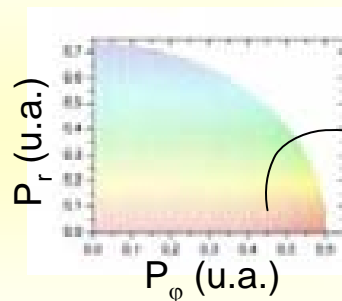
$$H(R, r, \theta, P_R, P_r, P_\theta) = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left[ \frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2} \right] \frac{P_\theta^2}{2} + V(R, r, \theta) = E$$

$$(v_R, v_\theta) \longrightarrow (v_R, v_r, v_\theta) \longrightarrow (v_r/v_R, v_\theta/v_R)$$

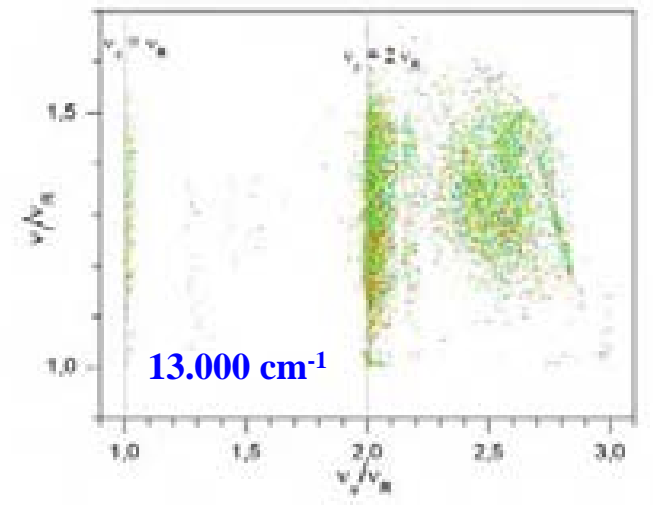
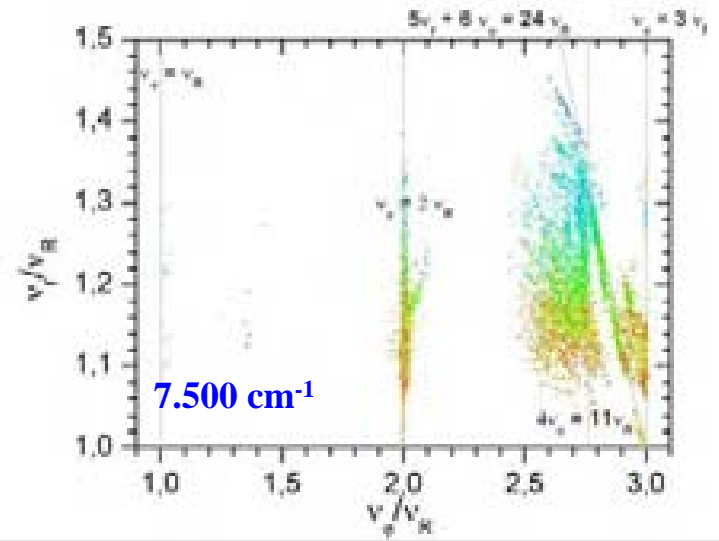
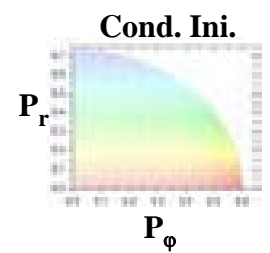
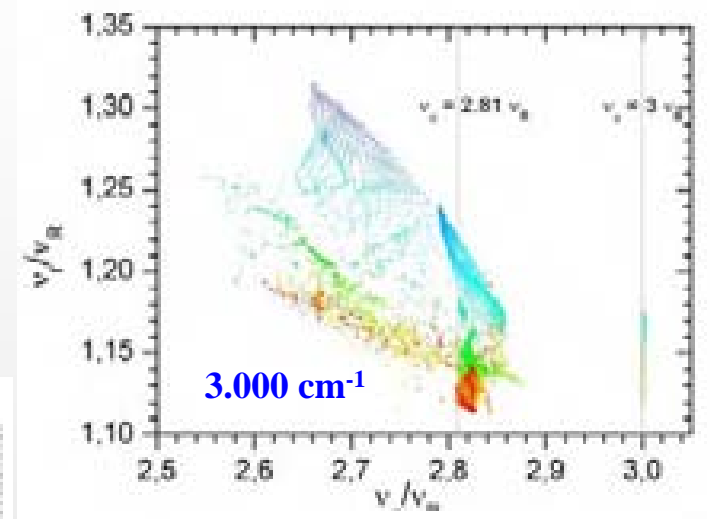
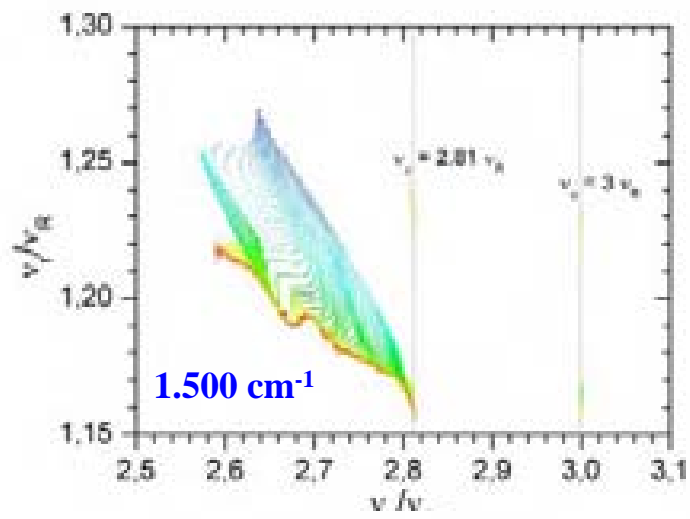


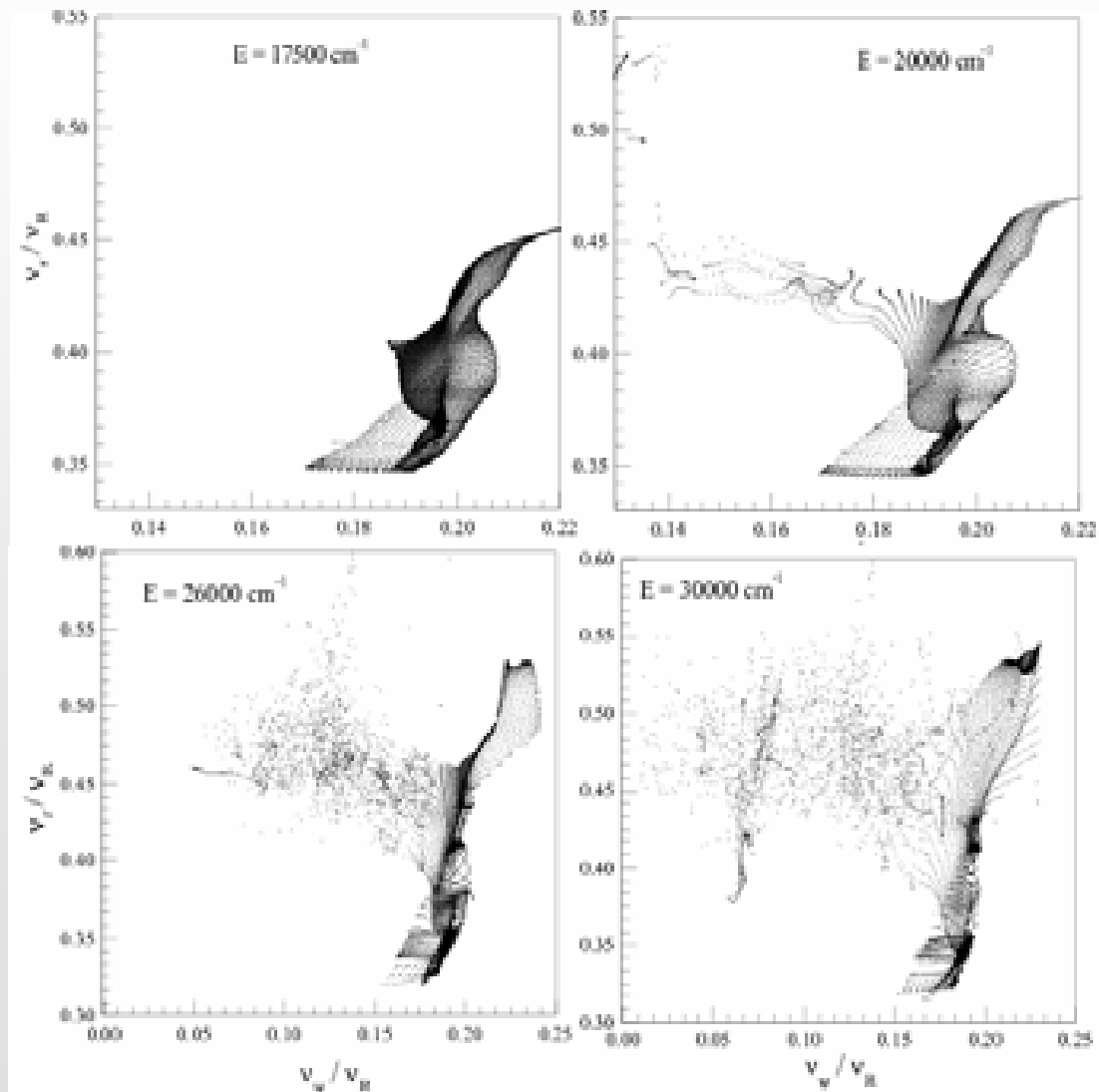
## Initial Conditions

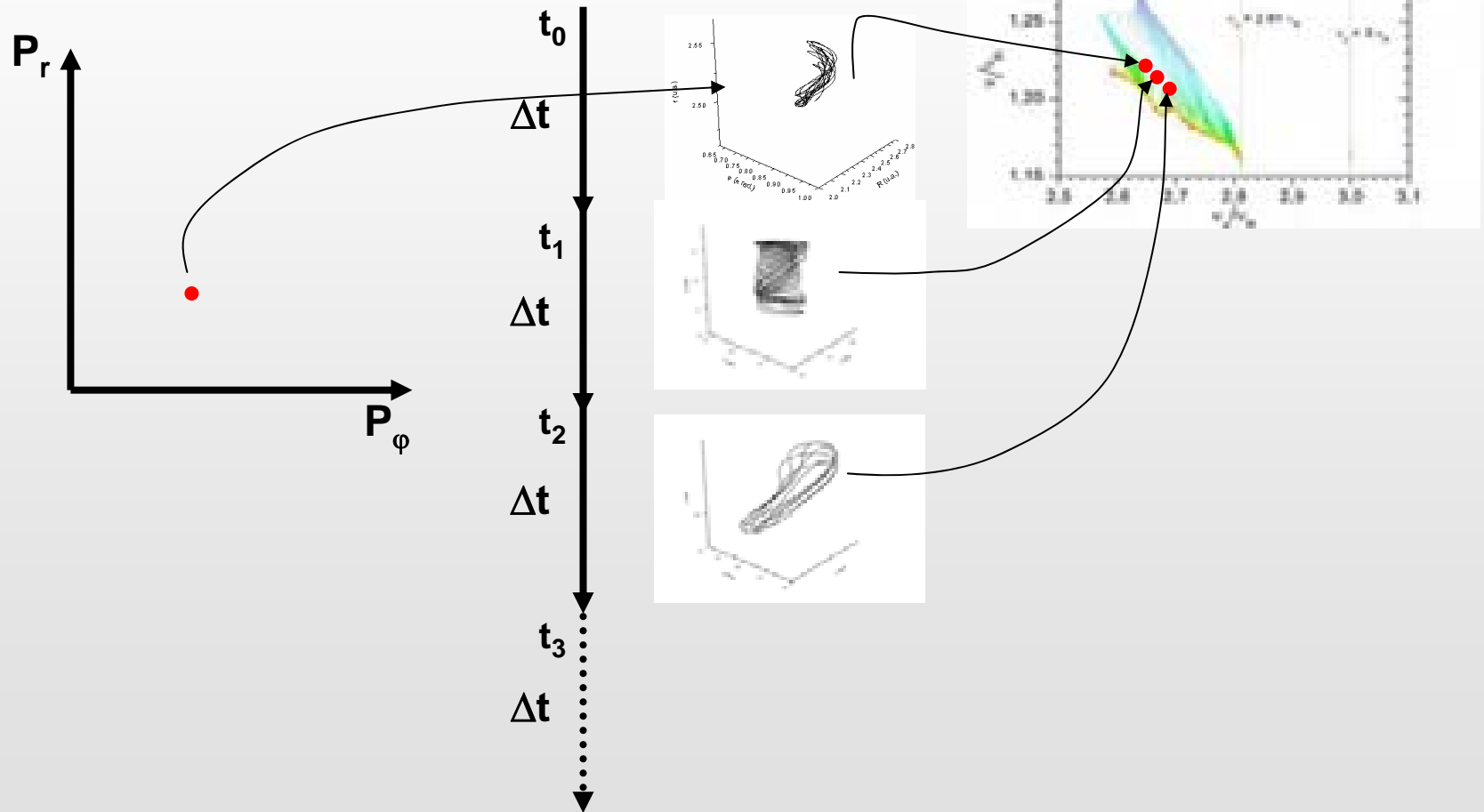
$$\begin{aligned} \theta_0 &= \theta_{eq.} \\ R_0 &= R_e(\theta_0) \\ r_0 &= r_{eq.} \end{aligned}$$



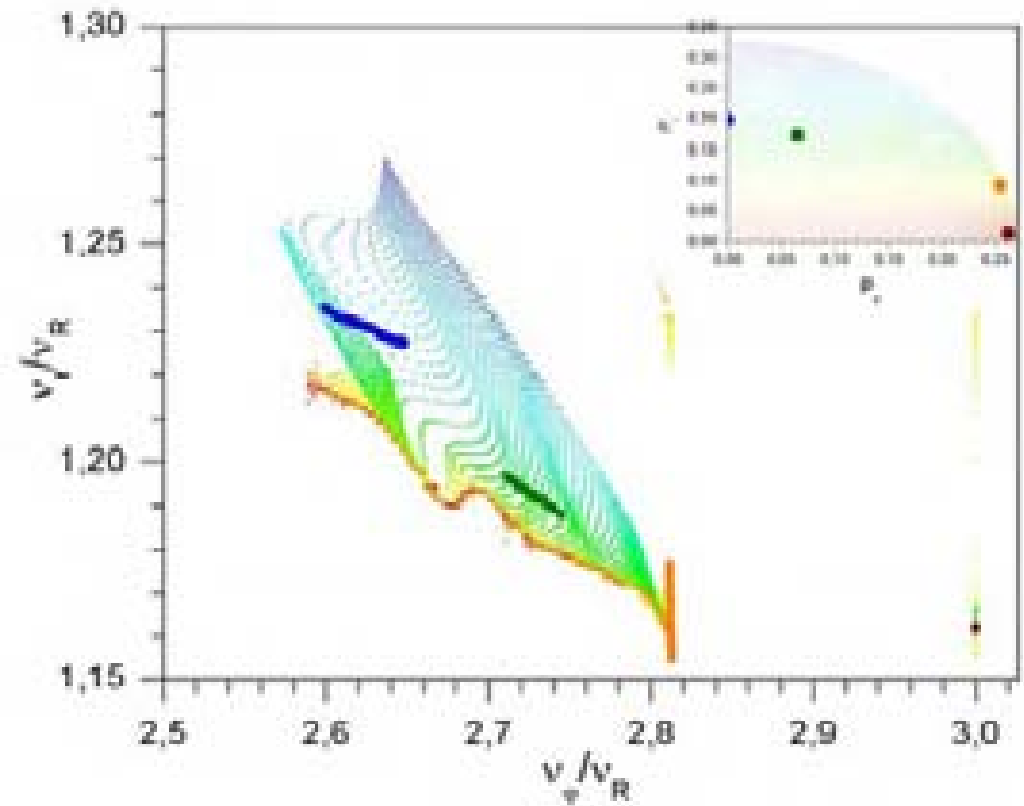
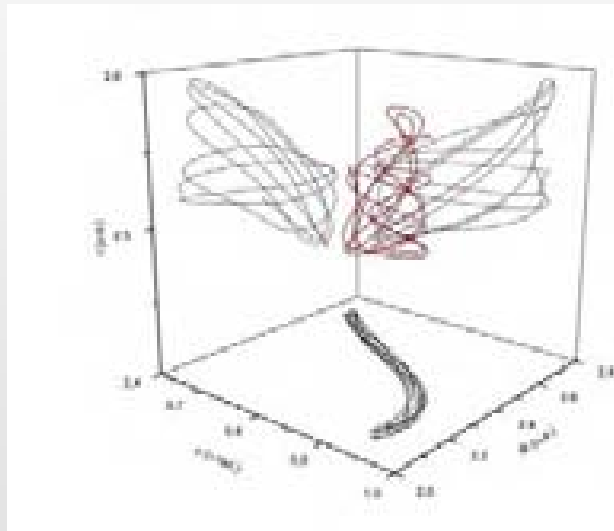
# HO<sub>2</sub>





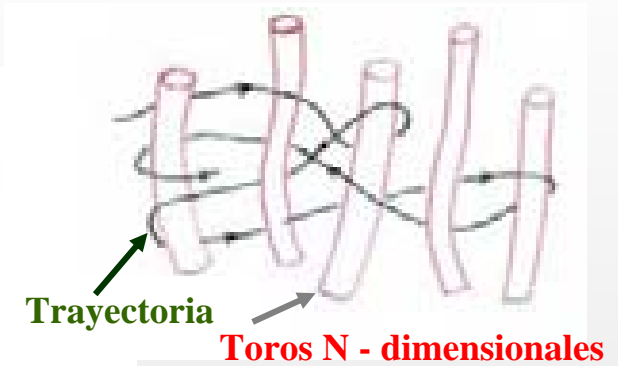
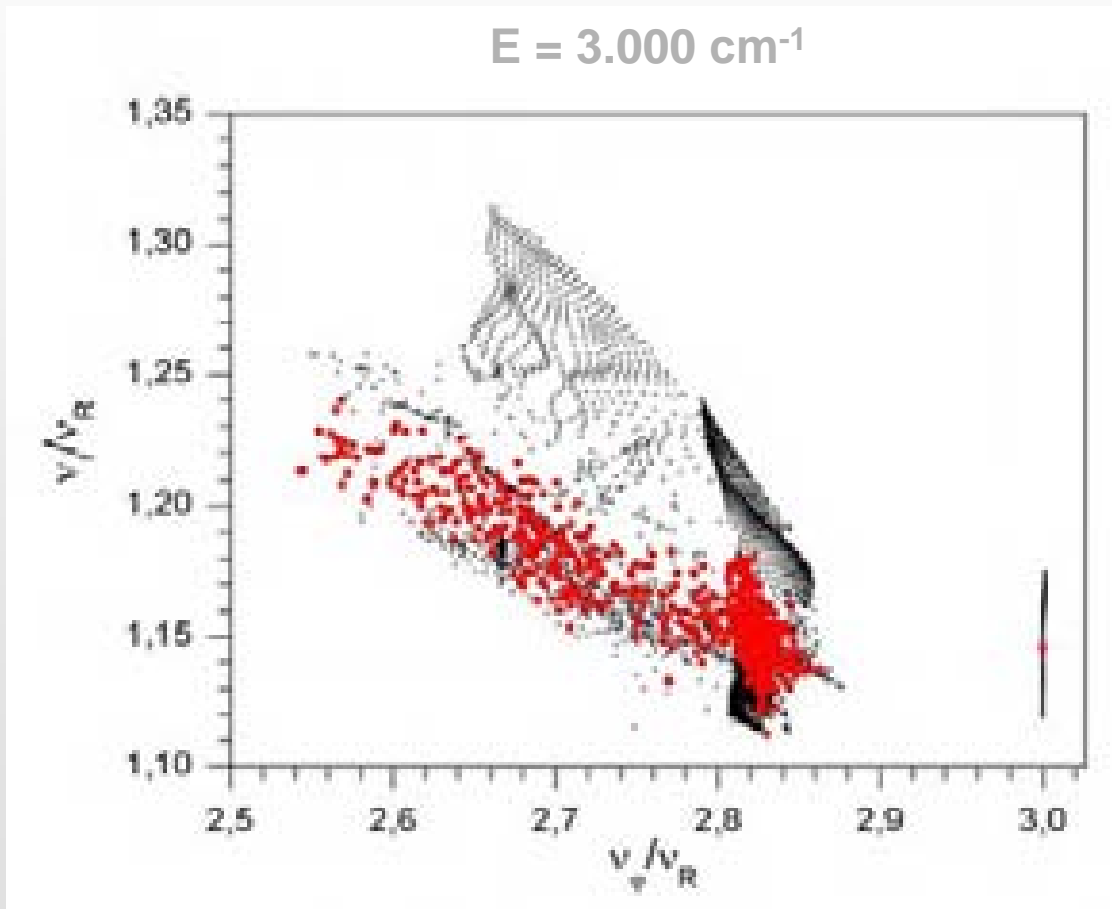


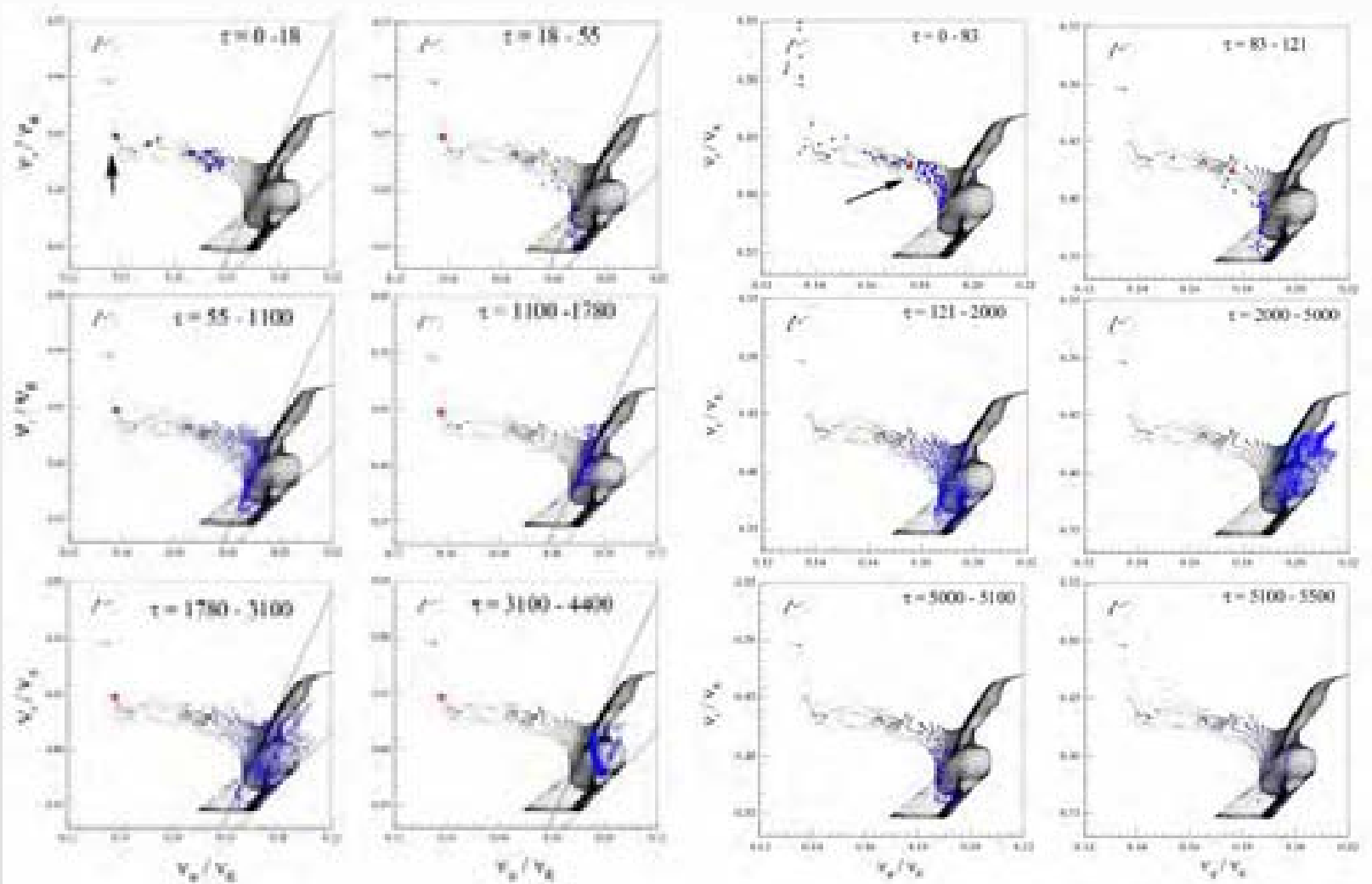
$E = 1.500 \text{ cm}^{-1}$





# HO<sub>2</sub>





# *Dinámica No Lineal de Vibraciones Moleculares*

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## Conclusions

📖 We have shown that FA can be used to efficiently extract dynamical information from chaotic trajectories of nonlinear molecular systems.

📖 The Local Frequency Analysis provides information about the main resonances of the systems.

📖 Finally, we would like to stress that the global picture provided by the frequency analysis makes research in intramolecular dynamics much more efficient, since it allows to target dynamically interesting regions using the map shown in this contribution.