



*De 2D a 3D: una breve historia de Dinámica
No Lineal de Sistemas Moleculares*

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ÍNDICE : *una breve historia de*

Sistemas Moleculares

Dinámica No Lineal de

De 2D

2,5 D

a 3D

ÍNDICE : *una breve historia de*

Sistemas Moleculares

Dinámica No Lineal de

De 2D

2,5 D

a 3D

Desde el punto de vista de la Dinámica No Lineal,

Las MOLECULAS son

SISTEMAS HAMILTONIANOS

Formados por una colección de

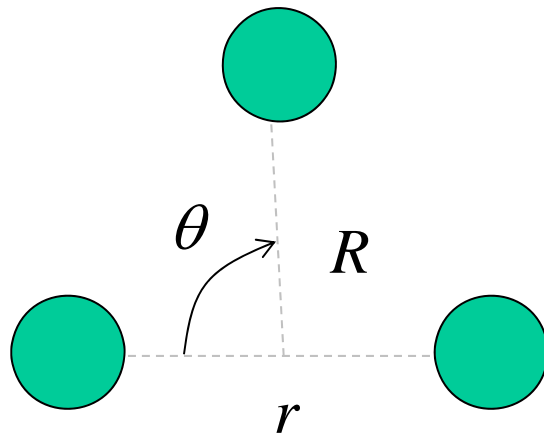
Osciladores anarmónicos acoplados

DINÁMICA CLASICA DE MOLÉCULAS TRIATÓMICAS

Vibraciones Moleculares



Movimiento de los núcleos



Coordenadas de Jacobi: r, R, θ

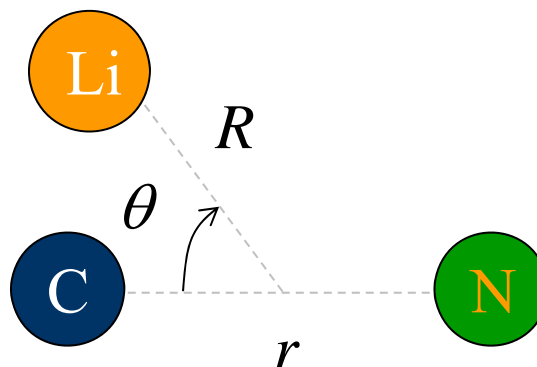
Potencial: $V = V(r, R, \theta)$ 3 gdl

Si $r = \text{cte.}$



$V = V(R, \theta)$
Sistema 2 gdl

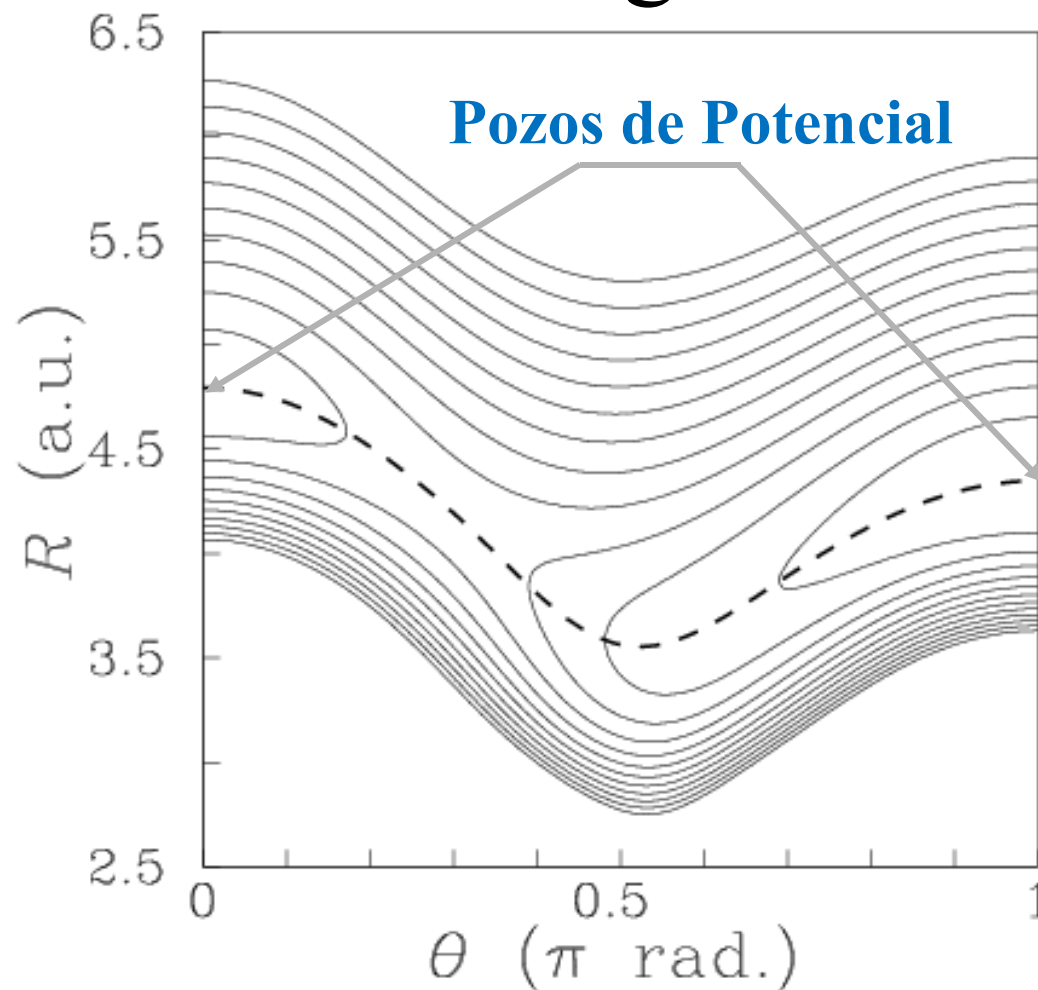
SISTEMA MOLECULAR **LiCN**



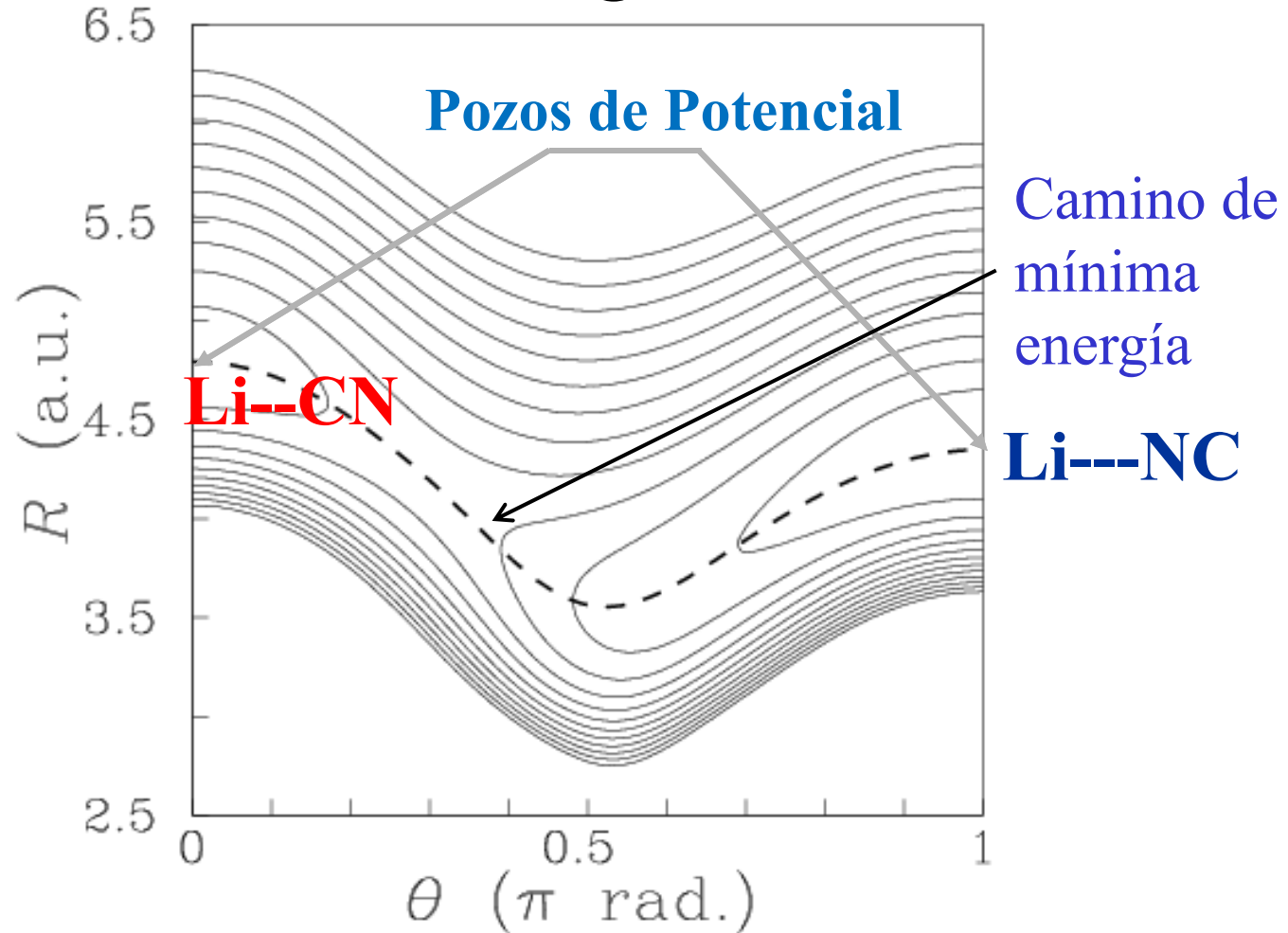
$$H(R, r, \theta, P_R, P_r, P_\theta) = \frac{P_R^2}{2\mu_1} + \frac{P_r^2}{2\mu_2} + \left[\frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2} \right] \frac{P_\theta^2}{2} + \boxed{V(R, r, \theta)} = \mathbf{E}$$

$$V(R, r, \theta) = V(R, \theta) + M(r)$$

LiNC/LiCN Energía Potencial 2D

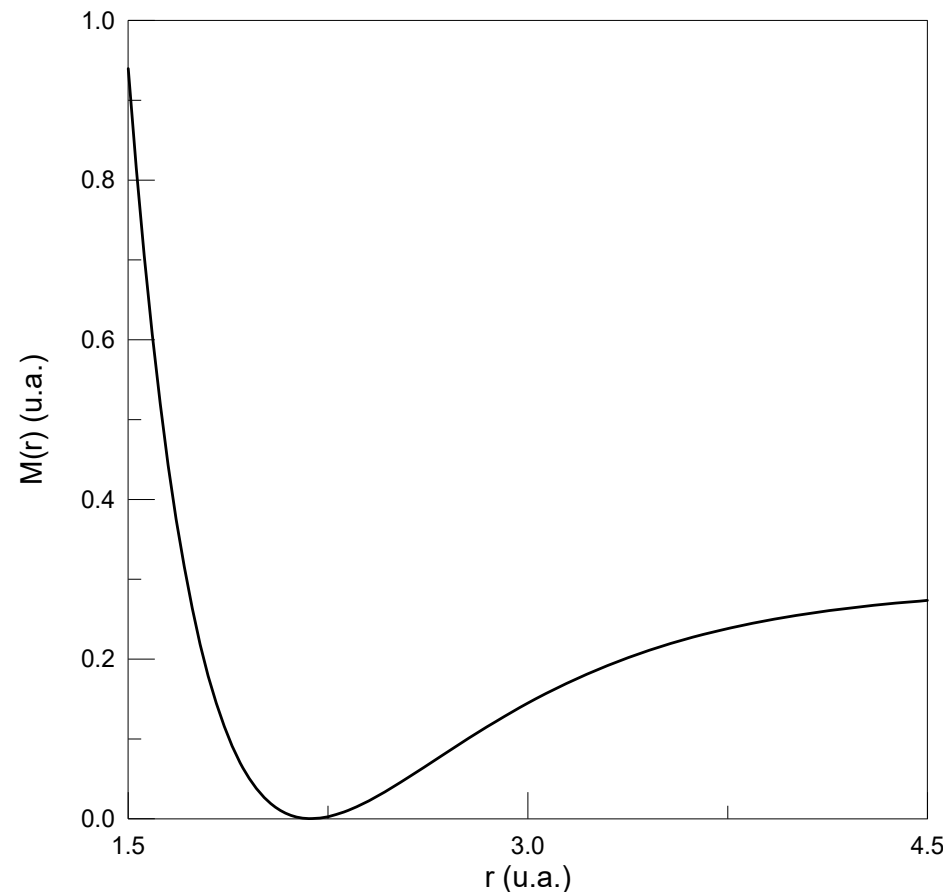


LiNC/LiCN Energía Potencial 2D



Energía Potencial para el movimiento C-N: $M(r)$

$$M(r) = d(1 - e^{-a(r_e - r)})^2$$



$$d = 0.29135 \text{ u.a.}$$

$$a = 1.4988 \text{ u.a.}$$

$$r_e = 2.186 \text{ u.a.}$$

Ecuaciones del movimiento de Hamilton

(2 grados de libertad $r = \text{cte}$)

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

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}$$

$$q_1 \equiv R \quad q_2 \equiv \theta$$

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

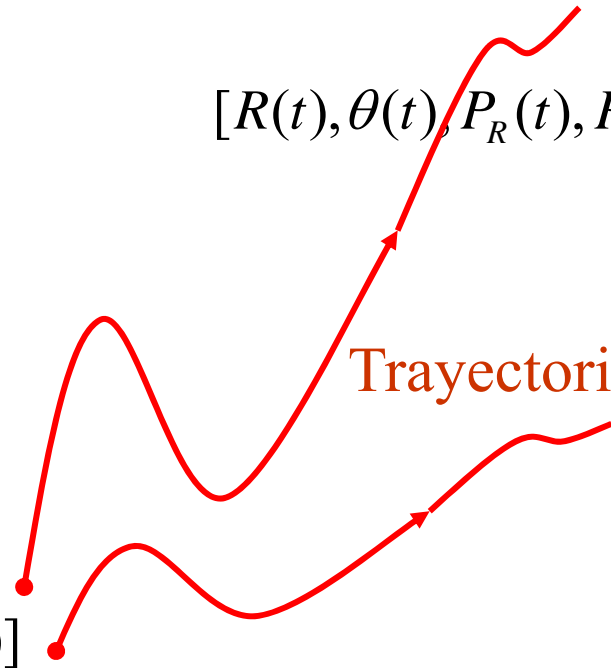
$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}$$

$$p_1 \equiv P_R \quad p_2 \equiv P_\theta$$

Trayectorias

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

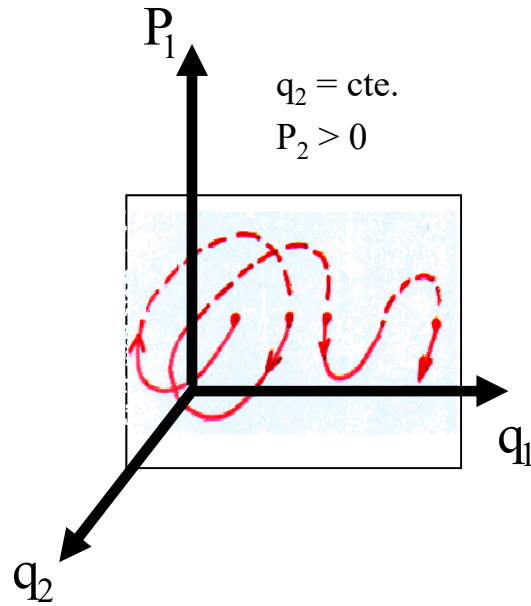
$$[R_2(t_0), \theta_2(t_0), P_{R_2}(t_0), P_{\theta_2}(t_0)]$$



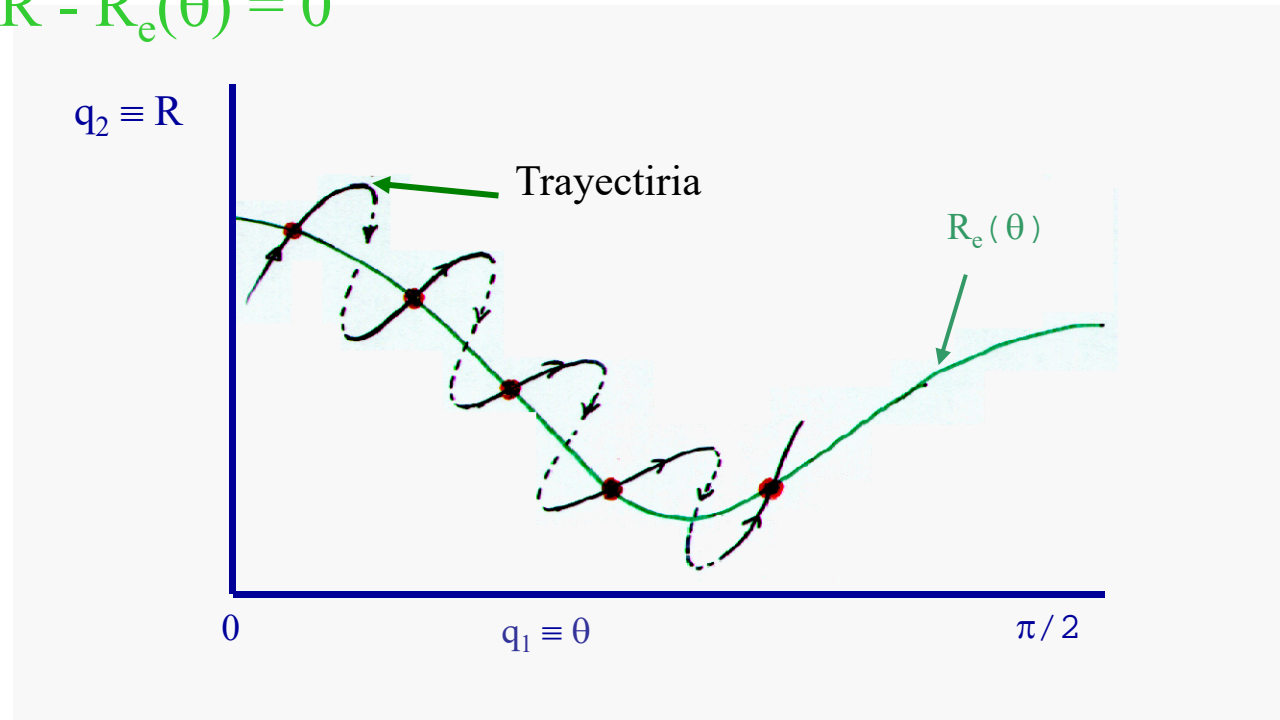
Podemos estudiar el comportamiento dinámico de las trayectorias y la estructura del espacio de fases mediante diferentes herramientas

- Superficie de Sección de Poincaré
- Mapa de Frecuencias
- SALI
- Geometrodinámica

Superficie de Sección de Poincaré



Superficie de Sección: **Camino de mínima energía**
 $R - R_e(\theta) = 0$



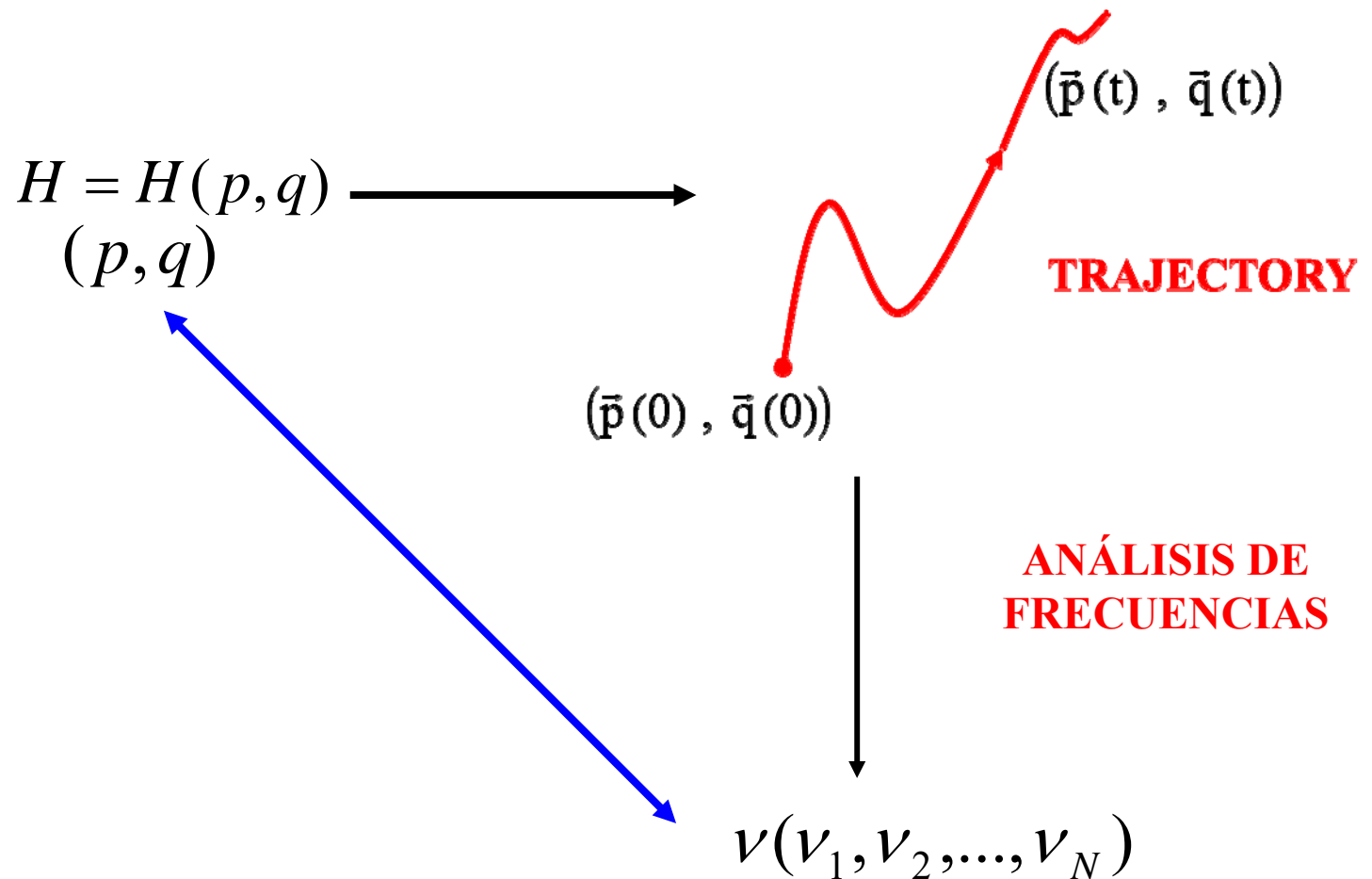
$$R = R_e(\theta) \Rightarrow$$

$$\rho = R - R_e(\theta) = 0$$

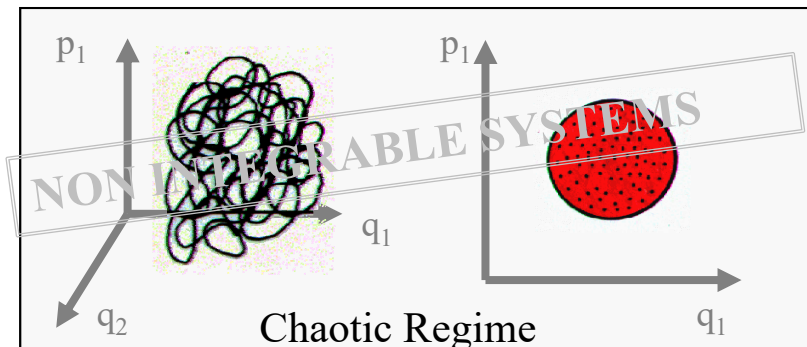
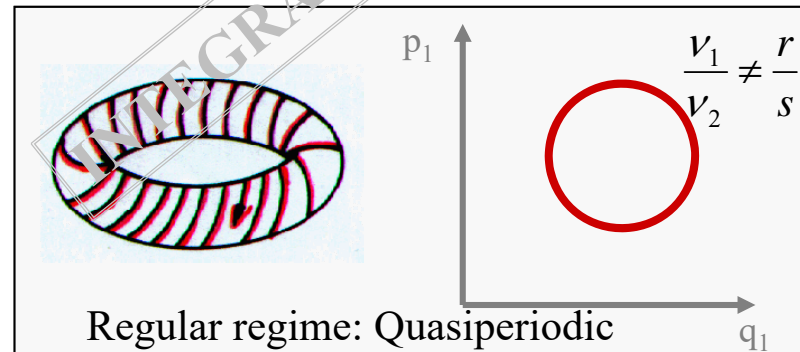
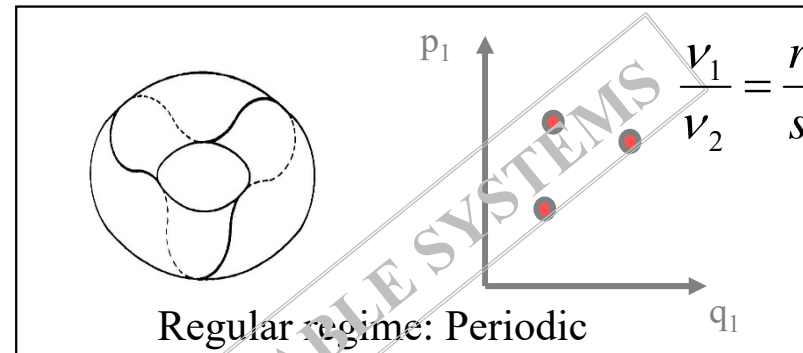
Cambio de
 coordenadas

$$\rho, P_\rho, \psi, P_\psi$$

MAPA DE FRECUENCIAS MP



ESTRUCTURA DEL ESPACIO DE FASES



J. Chem. Phys. 108 (1), 1 January 1998

**Local frequency analysis and the structure of classical phase space
of the LiNC/LiCN molecular system**

J. C. Losada, J. M. Estebaranz, and R. M. Benito

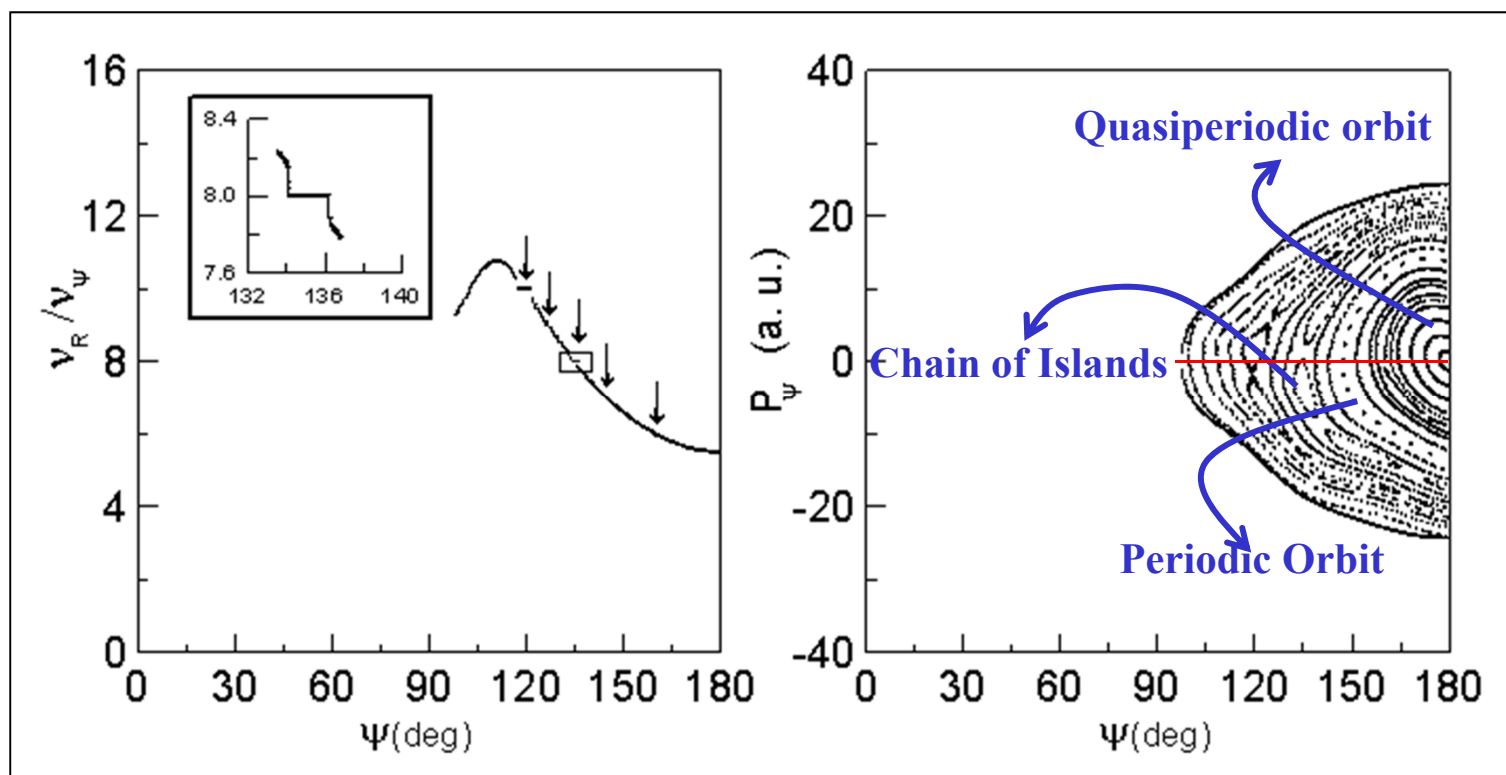
*Departamento de Física y Mecánica, Escuela Técnica Superior de Ingenieros Agrónomos,
Universidad Politécnica de Madrid, 28040 Madrid, Spain*

F. Borondo

Departamento de Química, C-IX, Universidad Autónoma de Madrid, Cantoblanco - 28049 Madrid, Spain

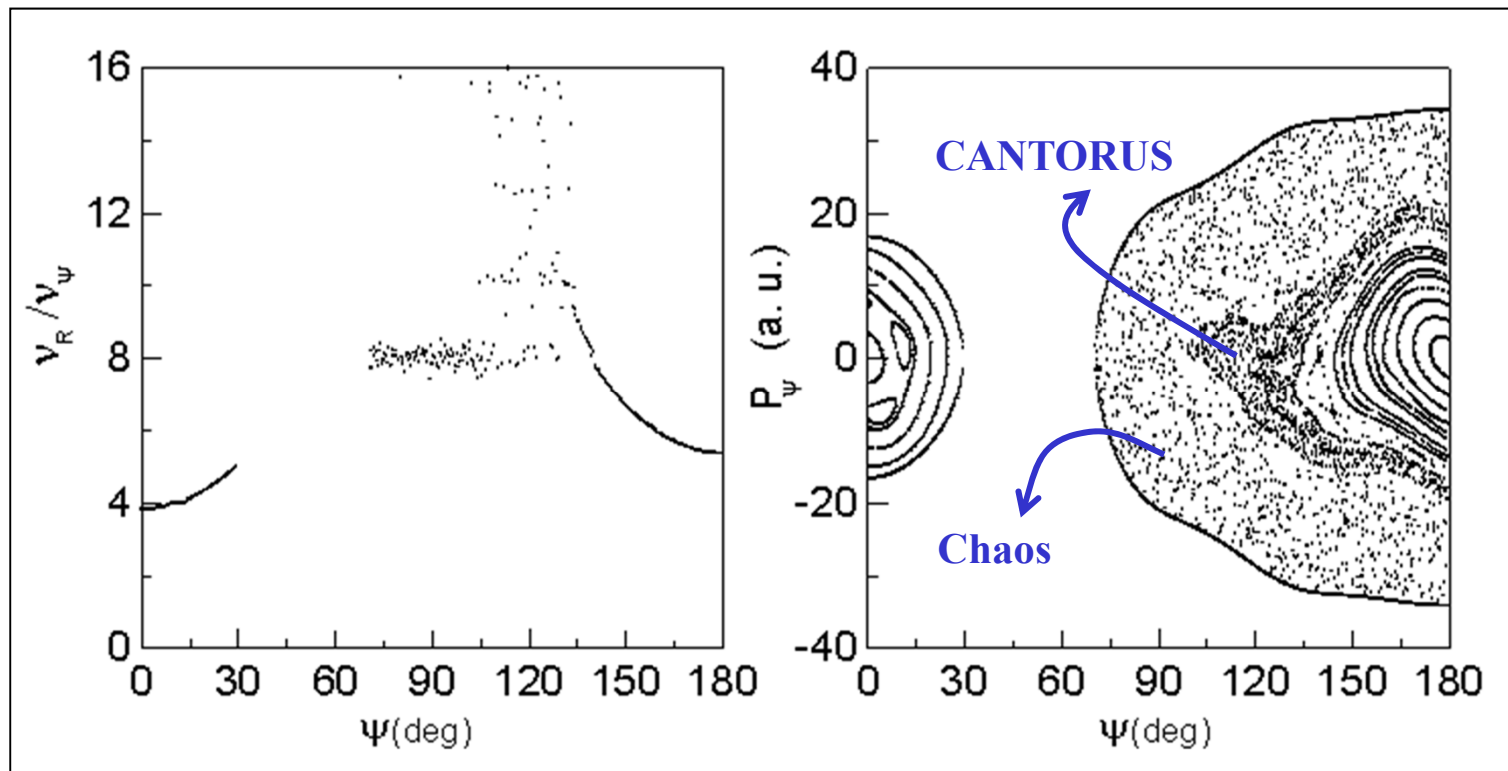
LiCN. 2D

MOVIMIENTO REGULAR



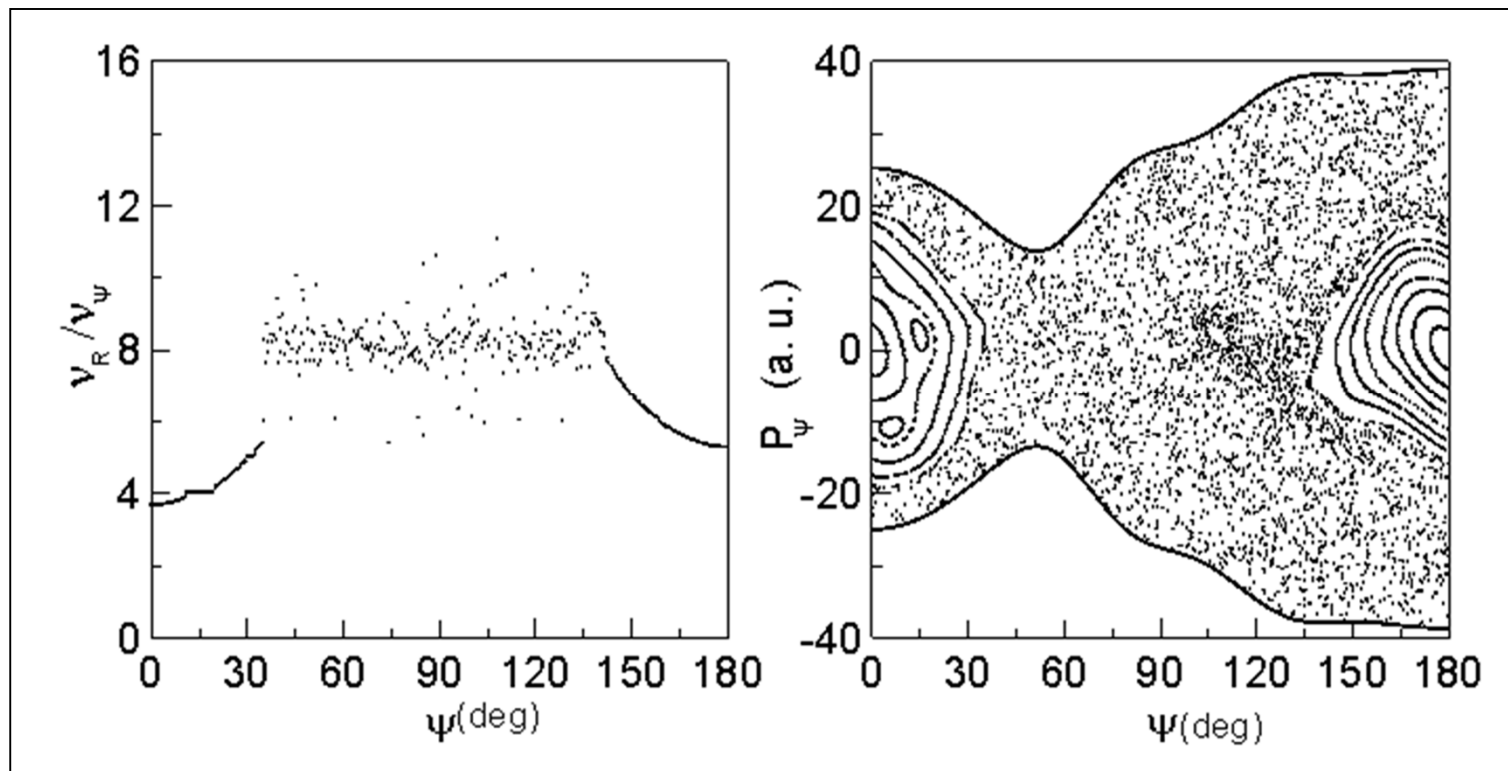
LiCN. 2D

MOVIMIENTO CAÓTICO



LiCN. 2D

MOVIMIENTO CAÓTICO



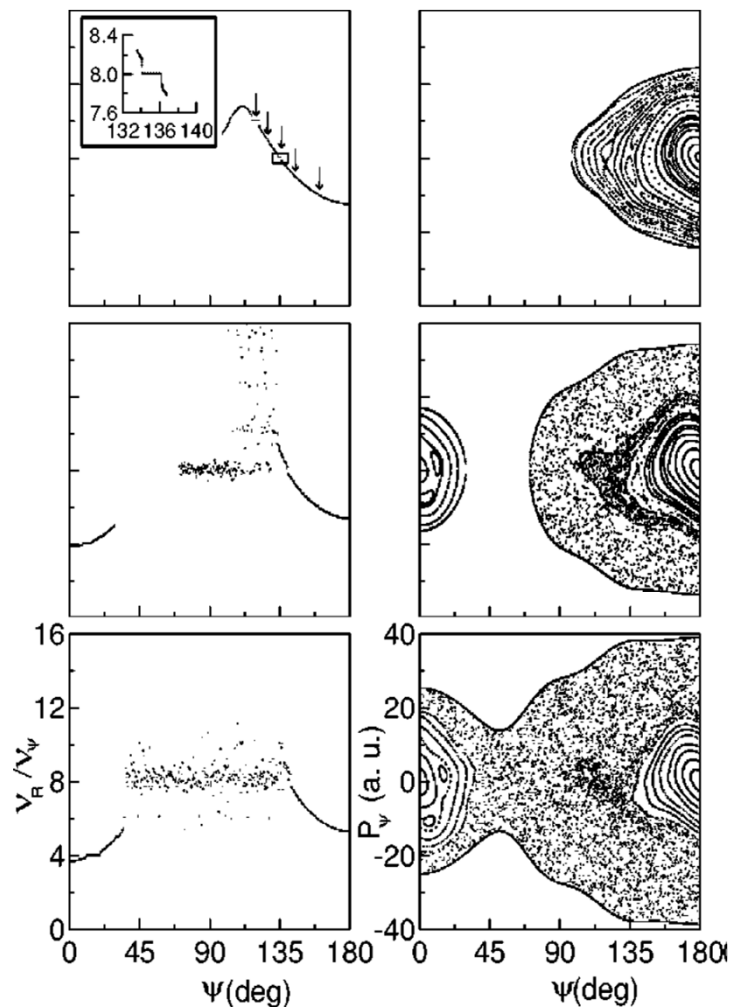


FIG. 1. Frequency ratio as a function of the initial angle ψ (left column) for an ensemble of trajectories started along the $P_\psi=0$ cut on the $\rho=0$ surface of section of LiNC/LiCN, and corresponding composite Poincaré surfaces of sections (right column), at different values of the vibrational energy: 1510.5 (top), 2964.7 (middle), and 3823.8 cm^{-1} (bottom).

$$D = \max\left(\frac{dv_\theta}{dt}; \frac{dv_R}{dt}\right)$$

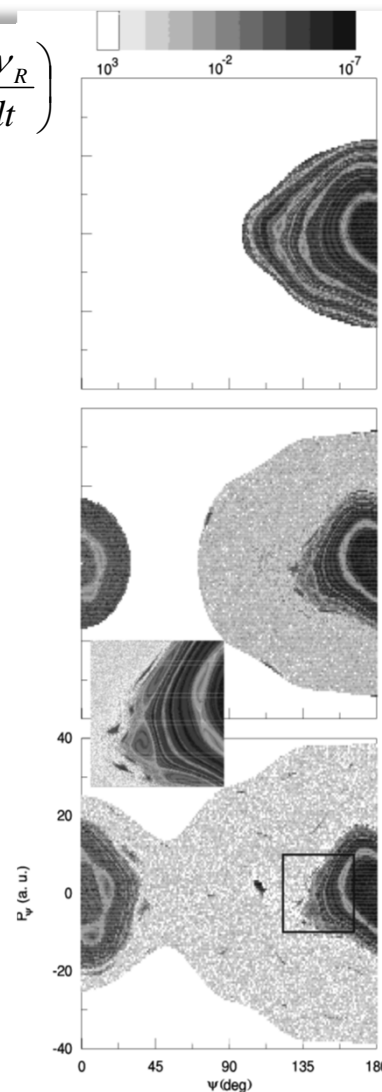


FIG. 12. Diffusion strength coefficient, defined as the initial value of $\max\{\partial v_R/\partial t, \partial v_\psi/\partial t\}$ in cm^{-1}/ps , calculated for trajectories initiated on a grid of points at the surface of the section for the same energies used in Fig. 1. The logarithmic scale of grays used is shown at the top of the figure.

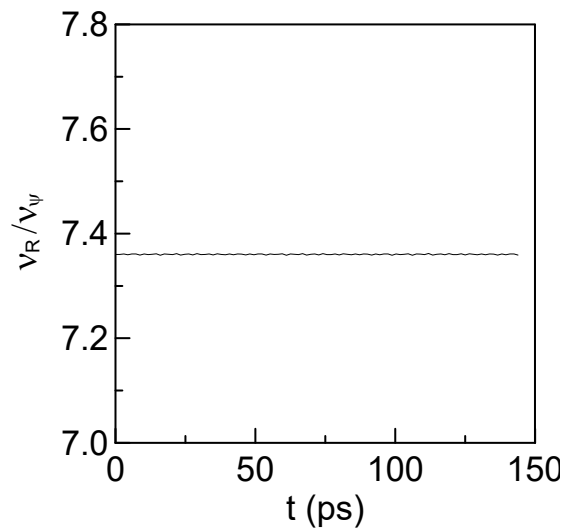
LiCN. 2D

Evolución temporal de la relación de frecuencias

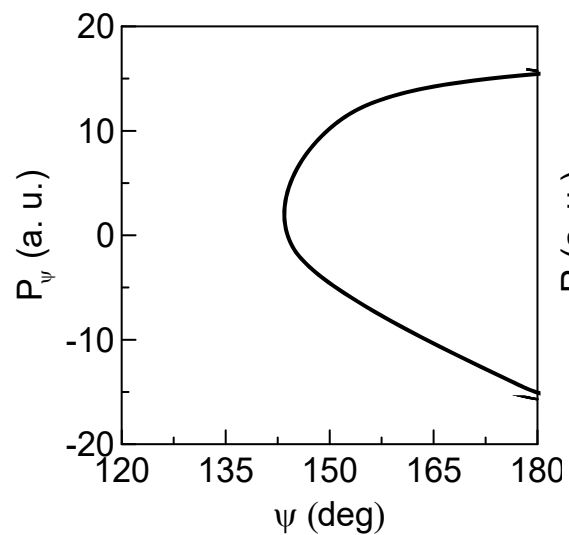
MOVIMIENTO REGULAR

$$\frac{V_R}{V_\psi} = cte$$

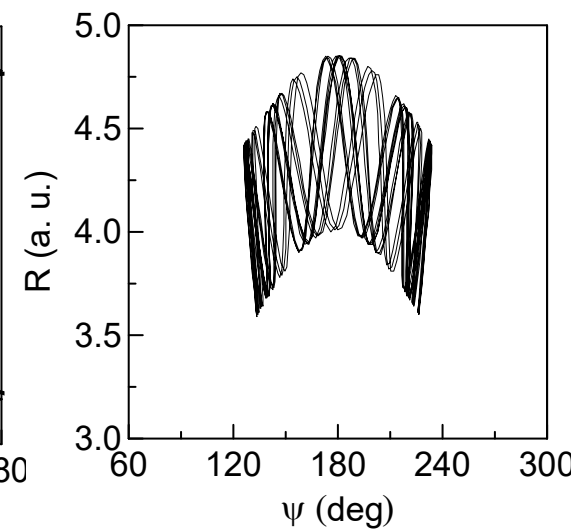
FA



PSS



Trajectory

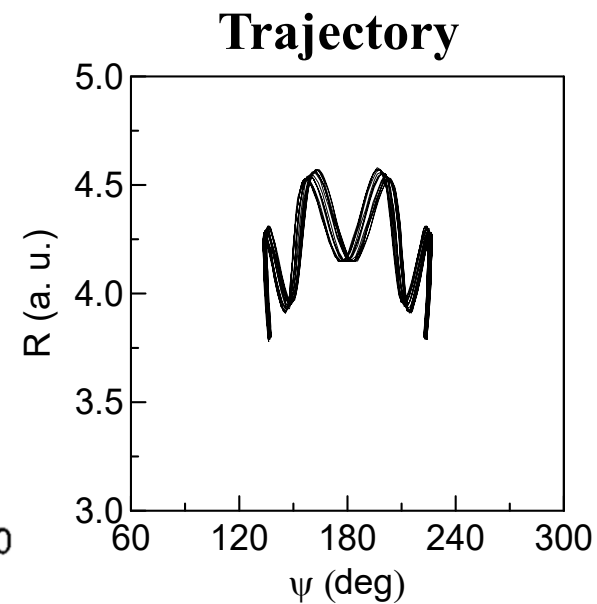
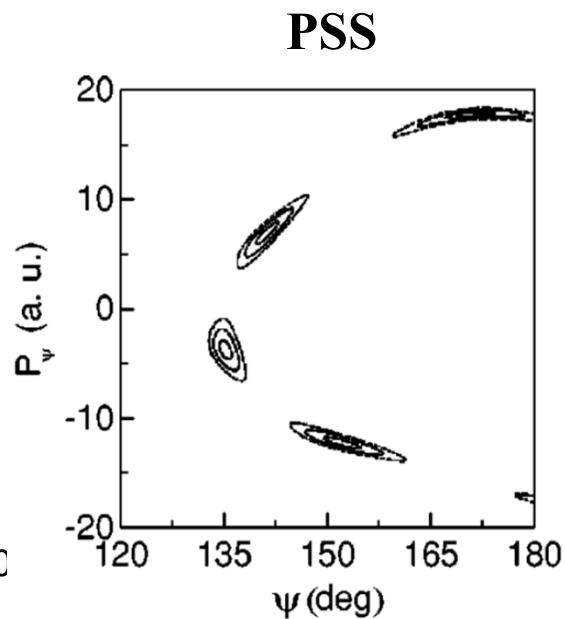
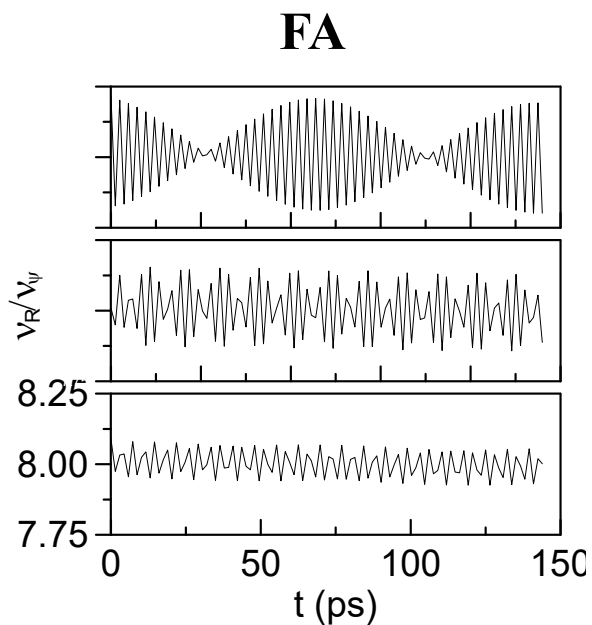


LiCN. 2D

Evolución temporal de la relación de frecuencias

MOVIMIENTO REGULAR

$$\frac{V_R}{V_\psi} = f(t) \text{ periodic function}$$

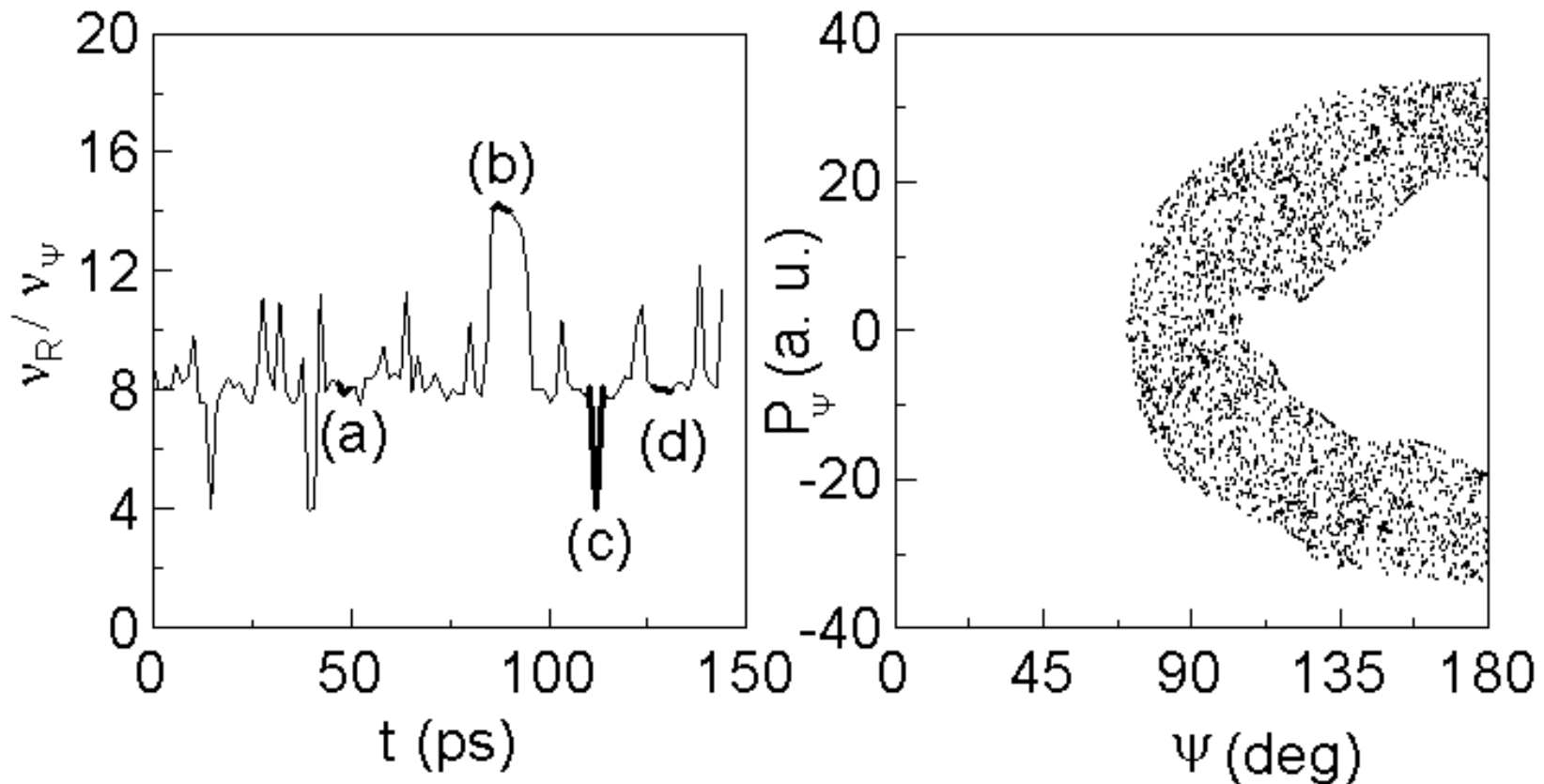


LiCN. 2D

Evolución temporal de la relación de frecuencias

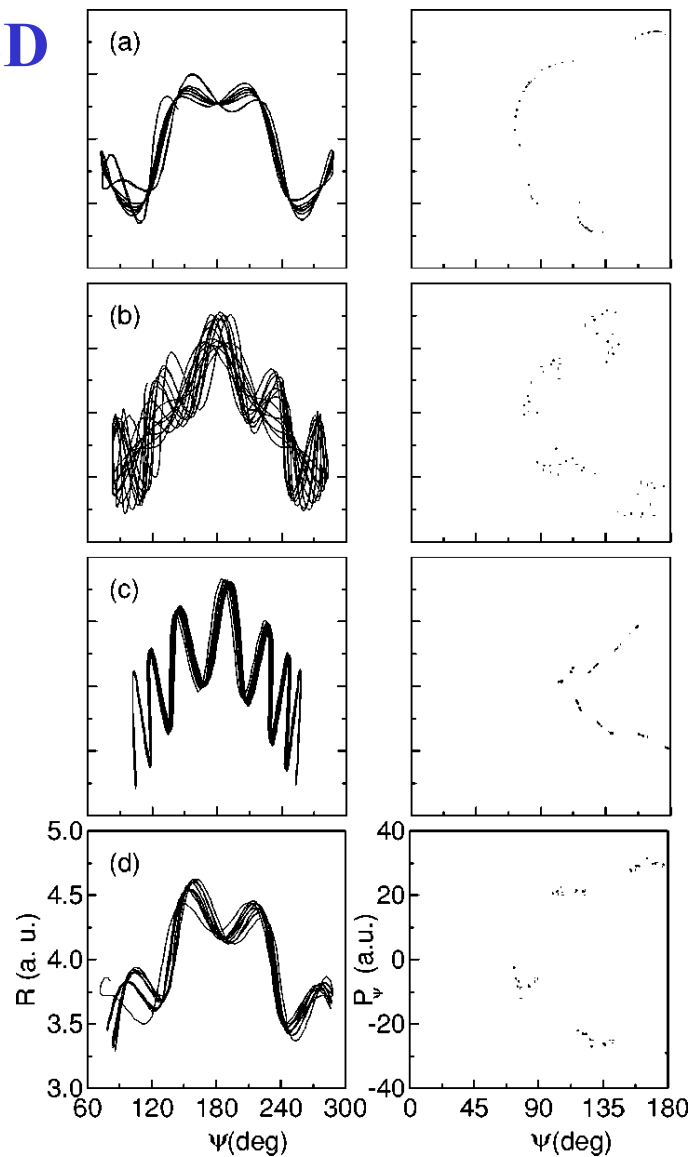
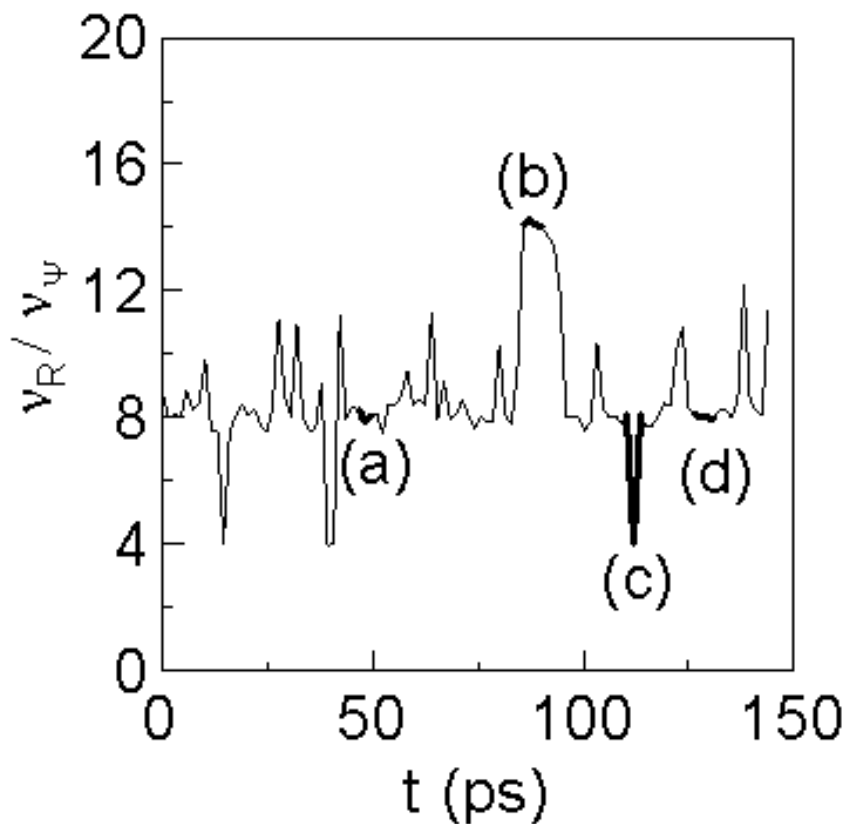
MOVIMIENTO CAÓTICO

$$\frac{\nu_R}{\nu_\psi} = f(t) \quad f(t) \text{ aperiodic function}$$



LiCN. 2D

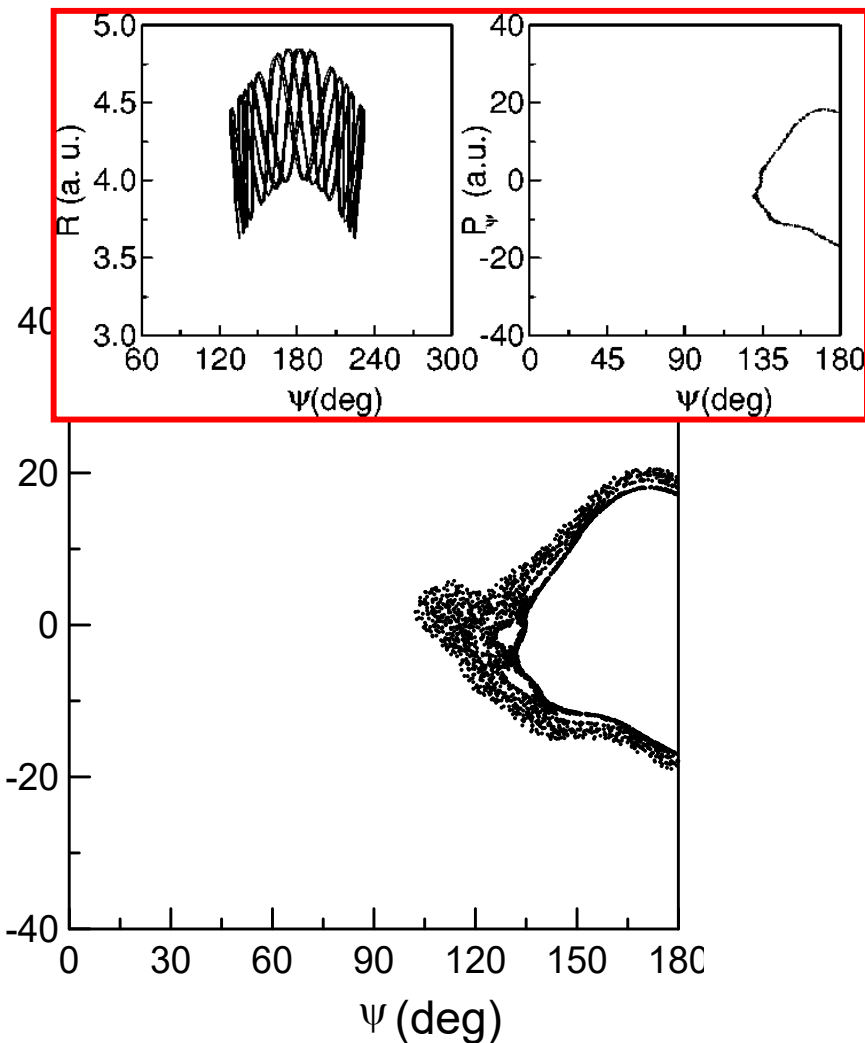
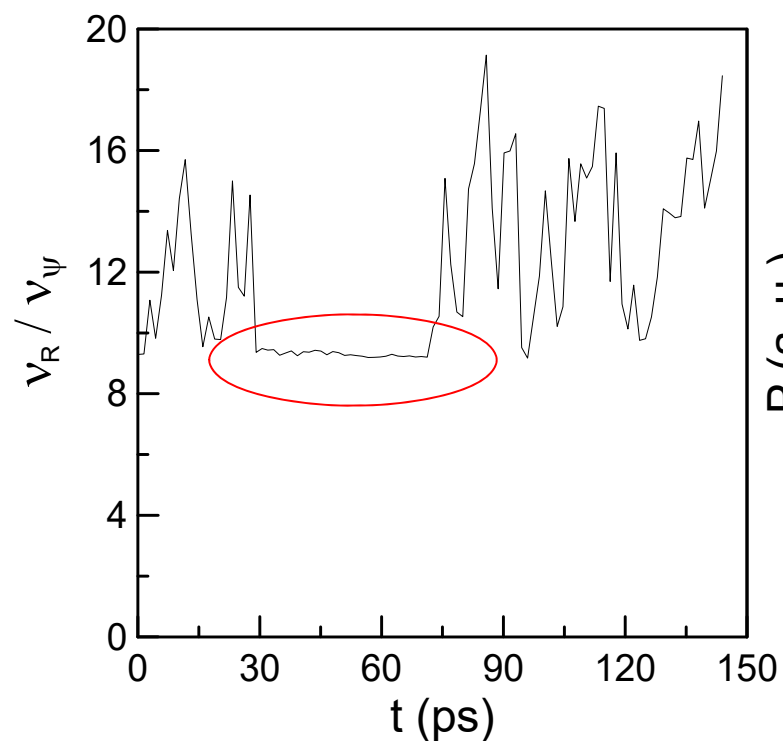
MOVIMIENTO CAÓTICO



LiCN. 2D

MOVIMIENTO CAÓTICO

Movimiento Confinado en el Cantoro

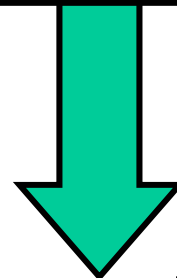


• **KAM-TOROS**



BARRERAS TOTALES

**DESTRUCCIÓN DE TOROS
ESTRUCTURA MULTIFRACTAL**



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



BARRERAS PARCIALES

PHYSICAL REVIEW E, VOLUME 65, 016213

Multifractal analysis of tori destruction in a molecular Hamiltonian system

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28040 Madrid, Spain*

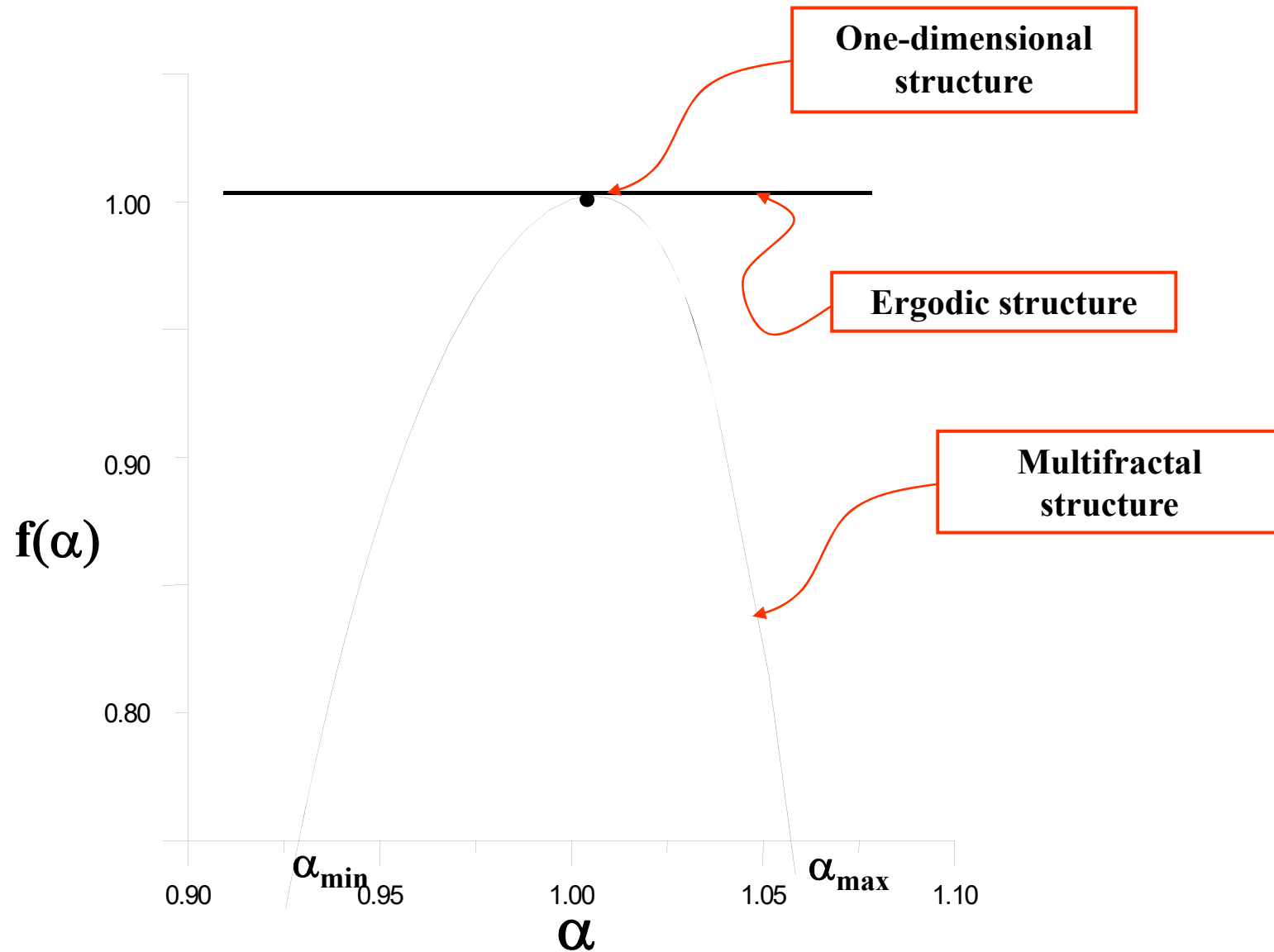
F. Borondo[†]

Departamento de Química, C-IX, Universidad Autónoma de Madrid, Cantoblanco 28049 Madrid, Spain

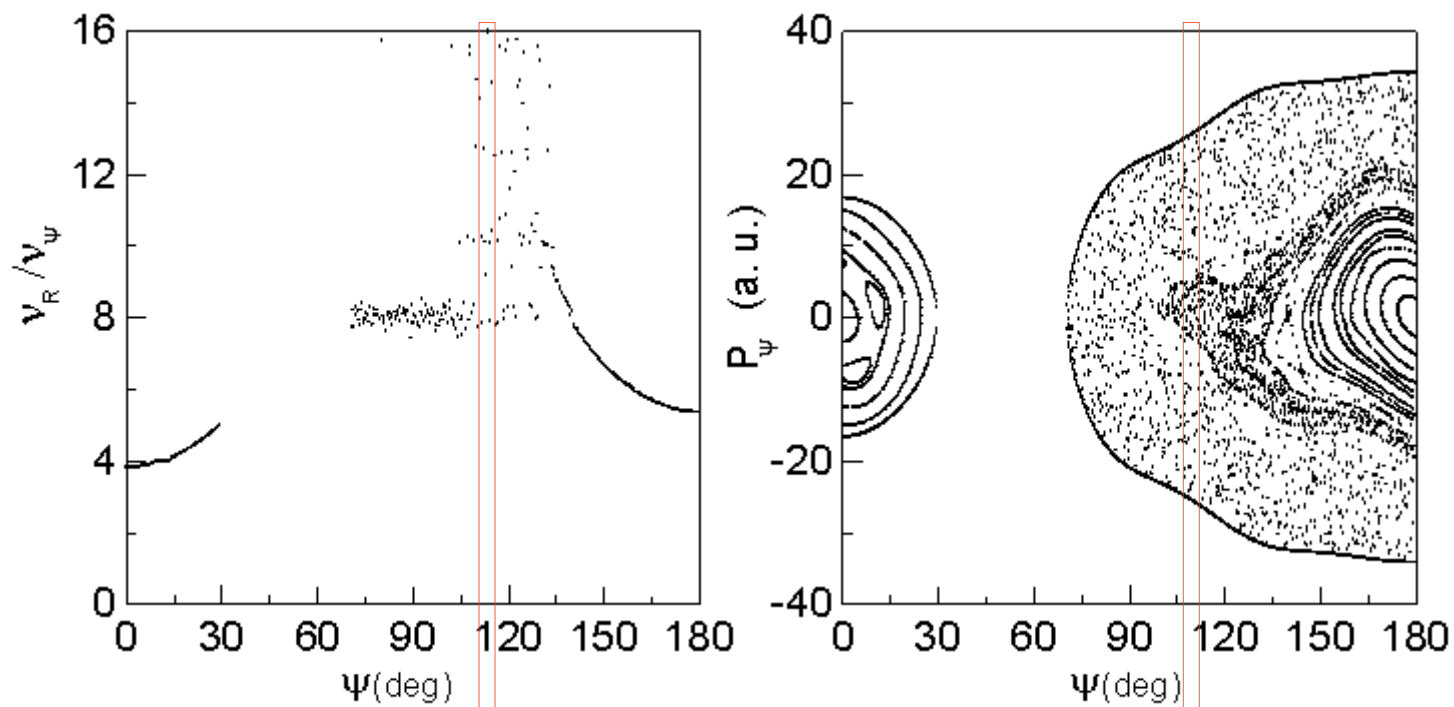
(Received 2 August 2001; published 20 December 2001)

In this paper, an analysis of the phase space structure of the isomerizing molecular system LiNC/LiCN, using Poincaré surfaces of section and frequency analysis, is presented. The scaling structure of the frequency map in the chaotic region next to the regular part corresponding to the stable linear isomer LiNC is studied using multifractal analysis. This approach is a way to characterize quantitatively the complexity in the mechanism of the tori destruction in a molecular Hamiltonian system that exhibits soft chaos as the vibrational energy of the system increases.

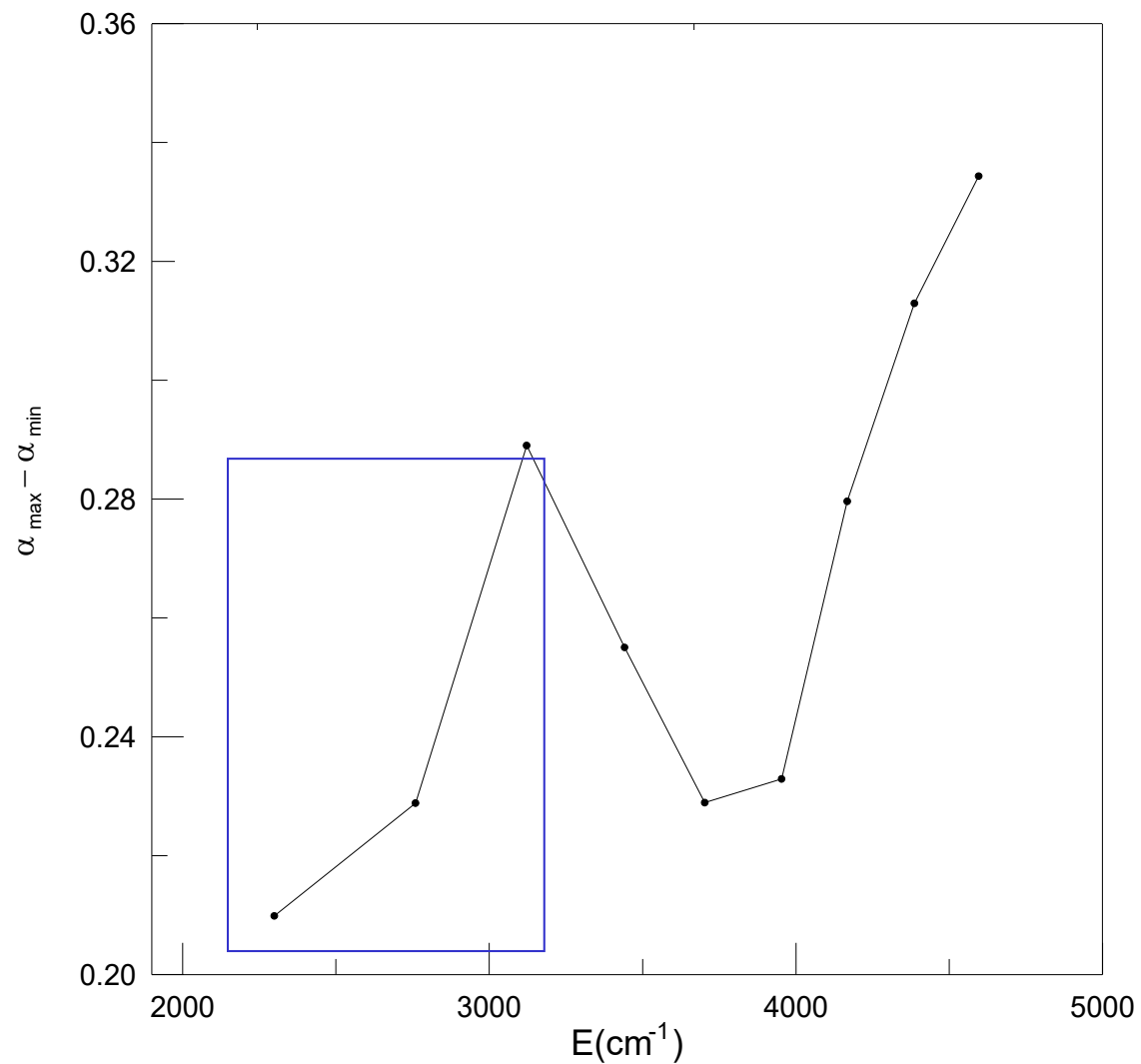
MULTIFRACTAL SPECTRUM



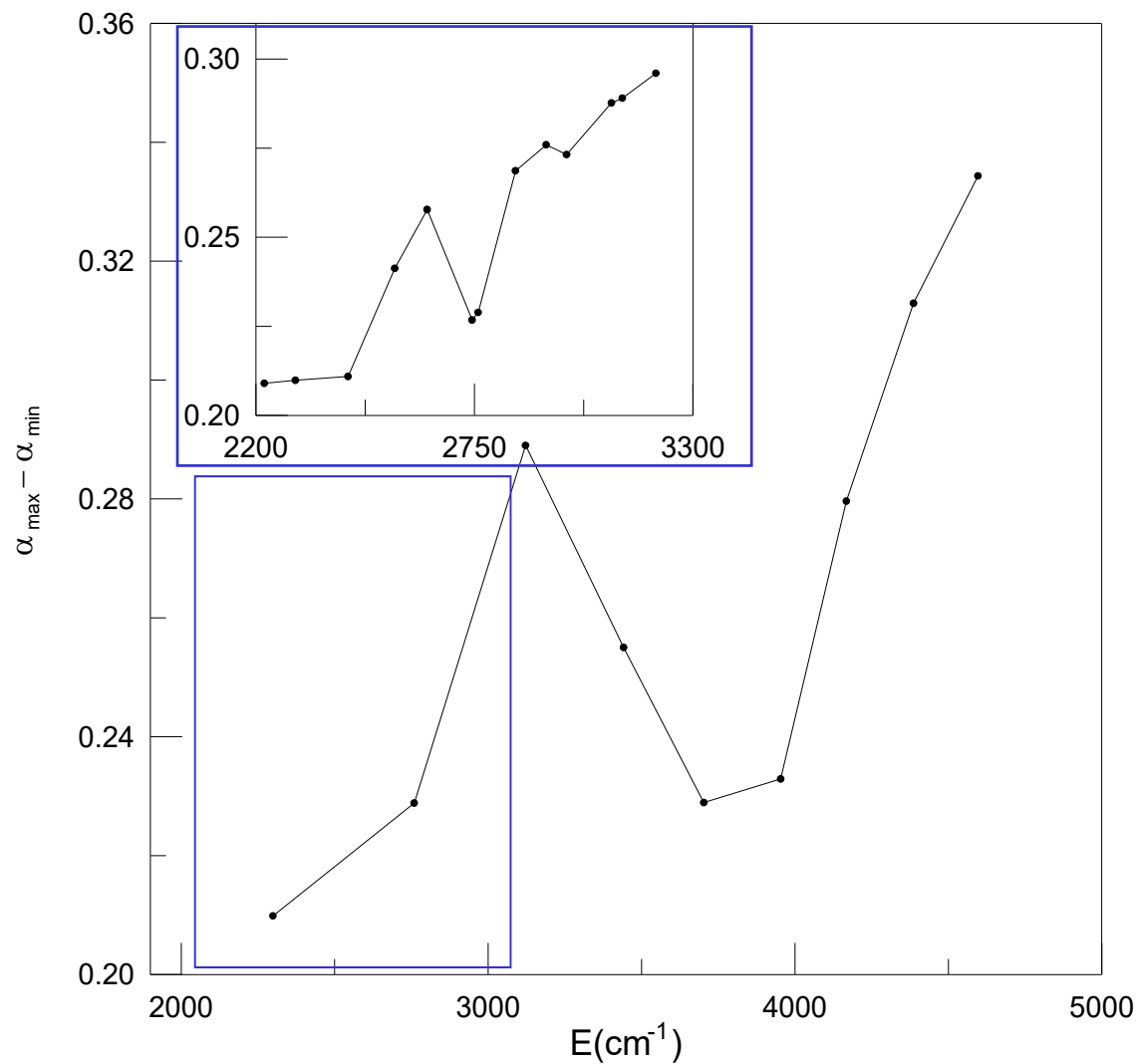
LiCN



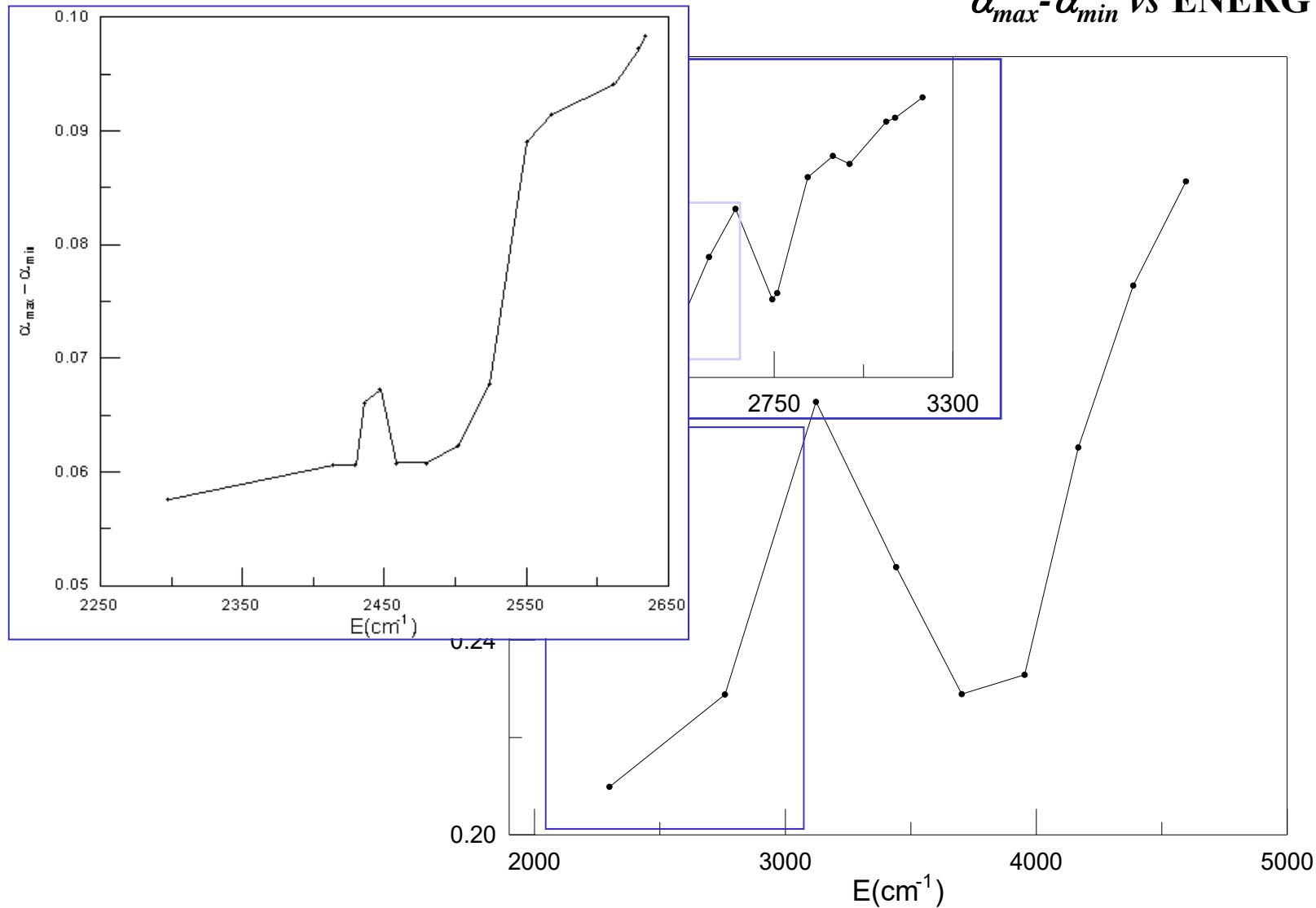
$\alpha_{max} - \alpha_{min}$ vs ENERGY



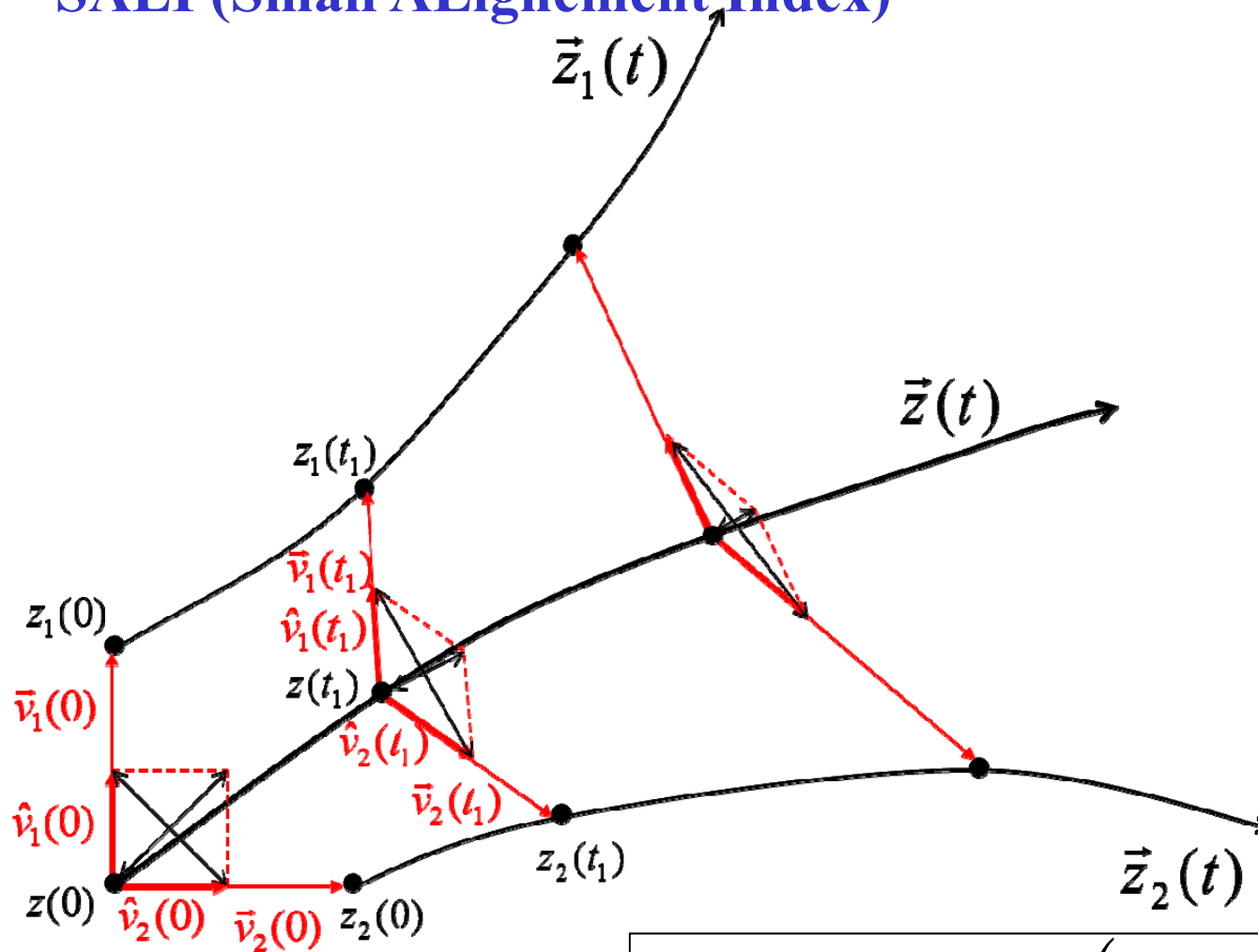
$\alpha_{max} - \alpha_{min}$ vs ENERGY



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



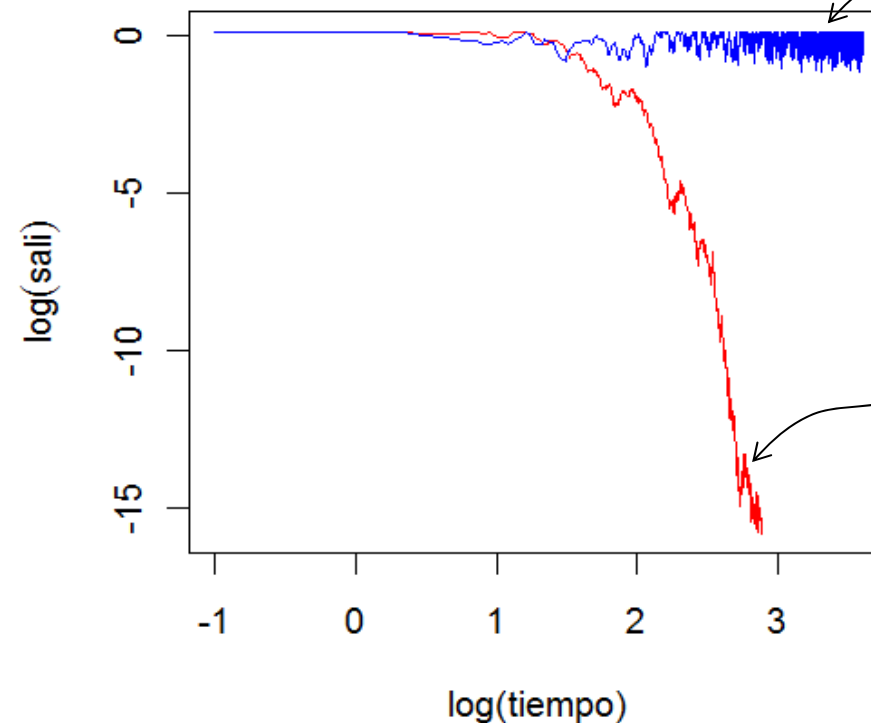
SALI (Small ALignment Index)



$$Sali(t) = \min\left(\left|\hat{v}_1 + \hat{v}_2\right|, \left|\hat{v}_1 - \hat{v}_2\right|\right)$$

$$SALI(z_0, t) = \min \left(\left| \vec{\hat{v}}_1 + \vec{\hat{v}}_2 \right|, \left| \vec{\hat{v}}_1 - \vec{\hat{v}}_2 \right| \right)$$

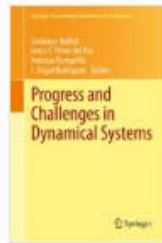
Regular



Chaotic

Asignamos a cada trayectoria el valor MINIMO de SALI

$$mSALI_T(z_0) = \min (SALI(z_0, t)) , t \in (0, T]$$




[Progress and Challenges in Dynamical Systems](#) pp 77-88 | [Cite as](#)

Analysis of the Full Vibrational Dynamics of the LiNC/LiCN Molecular System

Authors

[Authors and affiliations](#)

P. Benítez , J. C. Losada, R. M. Benito, F. Borondo

PHYSICAL REVIEW E **92**, 042918 (2015)

Using the small alignment index chaos indicator to characterize the vibrational dynamics of a molecular system: LiNC-LiCN

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³*Instituto de Ciencias Matemáticas (ICMAT), Cantoblanco, E-28049 Madrid, Spain*

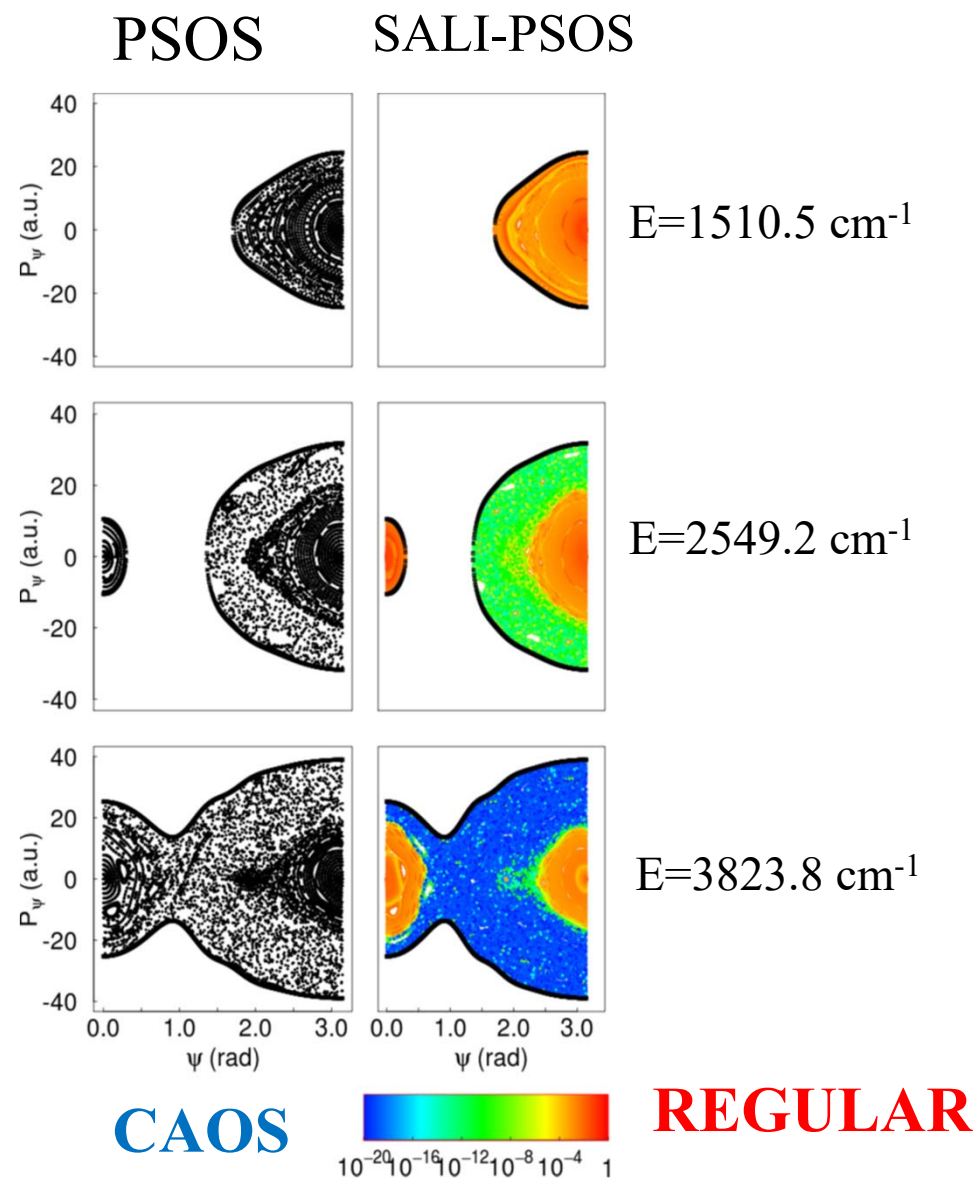
LINC/LICN- 2D

SALI-PSOS

Poincare Surface of Section
 colored by SALI

Definición:

A cada punto de la SSP se le asigna el color correspondiente al $mSALI_T$ de la trayectoria

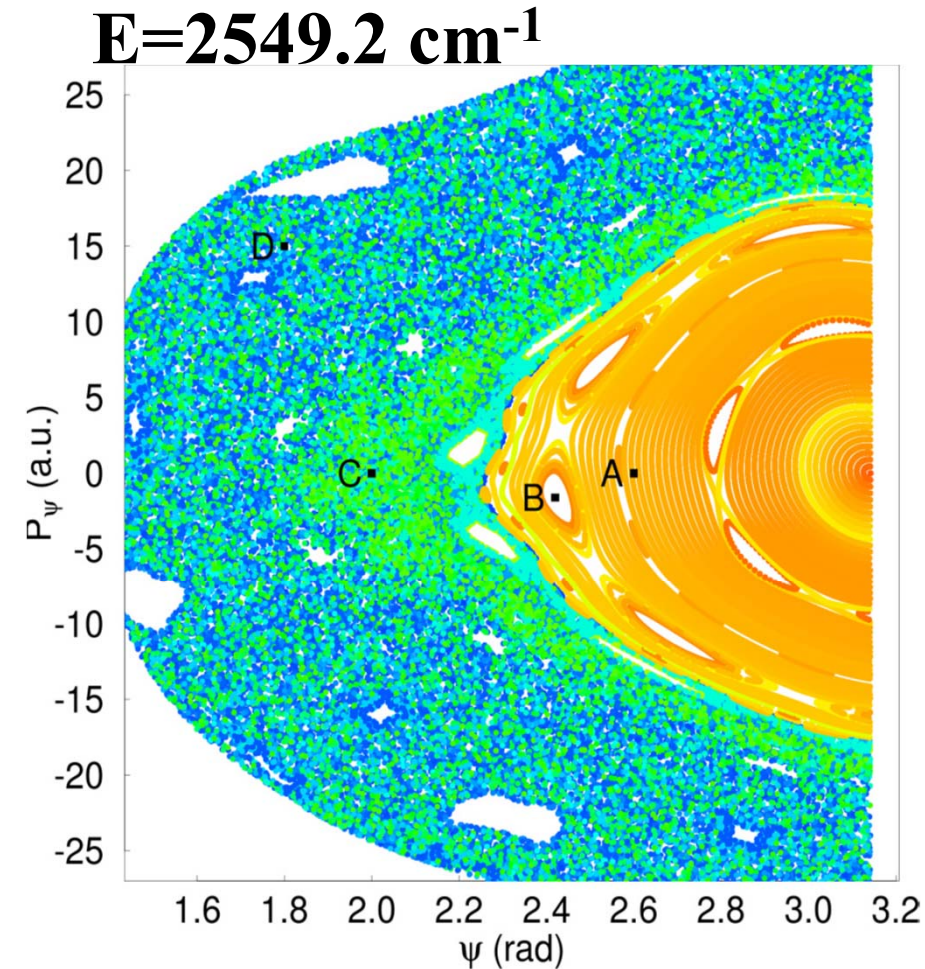


LINC/LICN- 2D

SALI-PSOS

Definición:

A cada punto de la SSP se le asigna el color correspondiente al $mSALI_T$ de la trayectoria

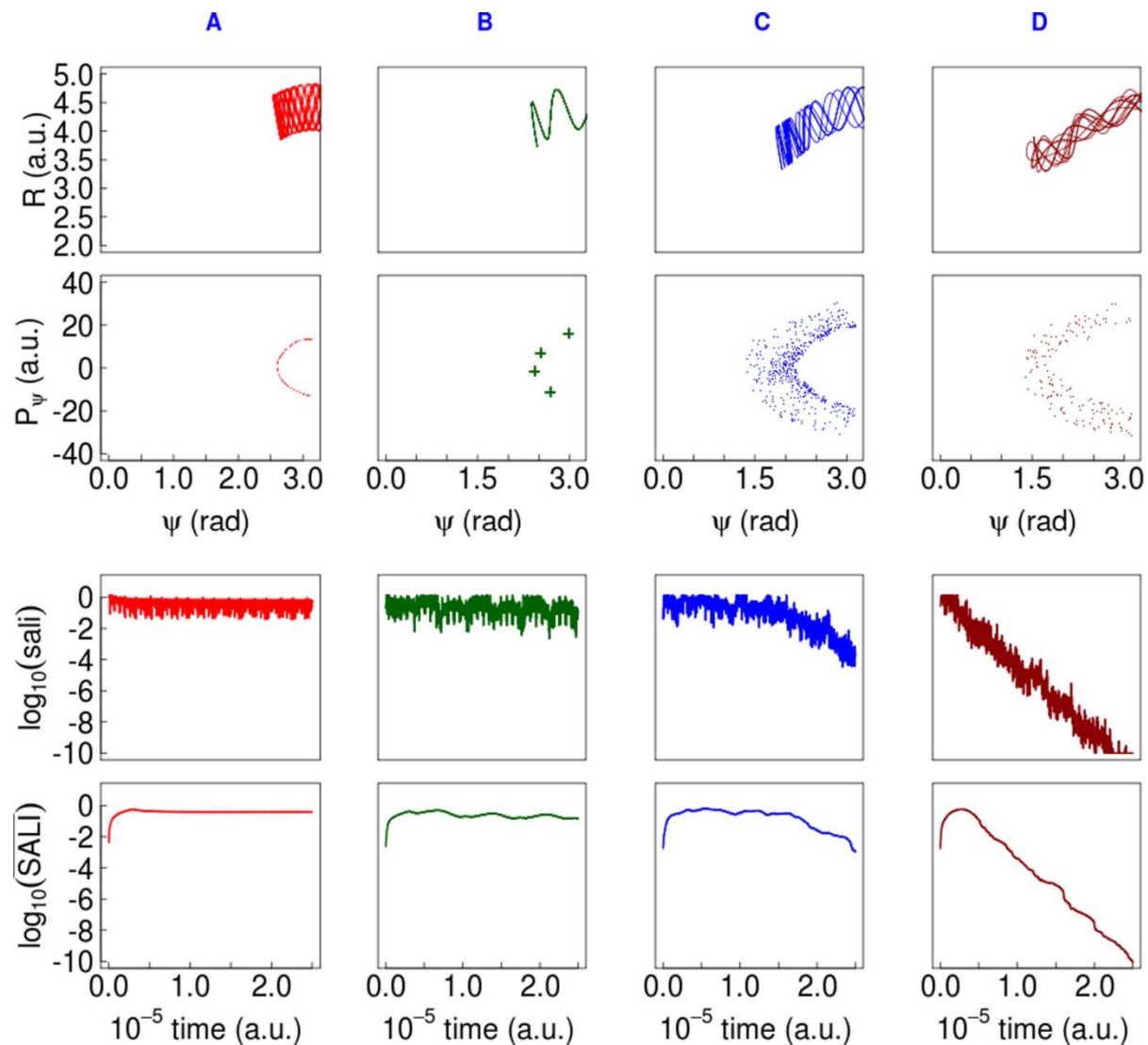
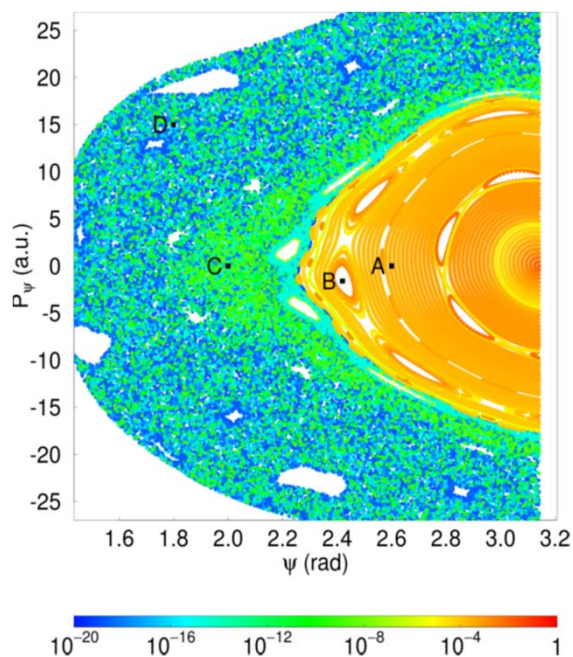


Caos

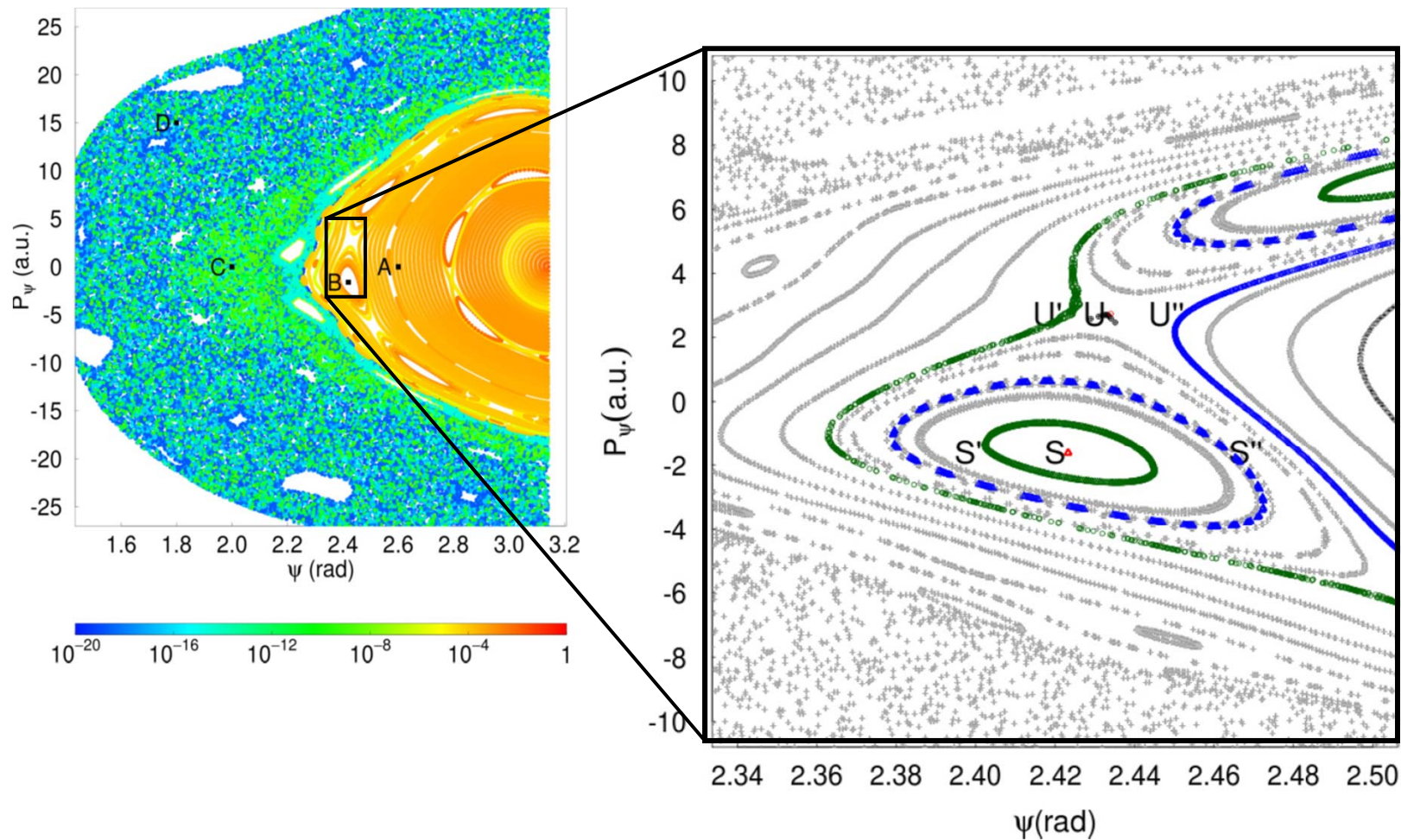
Regular

Diferentes trayectorias

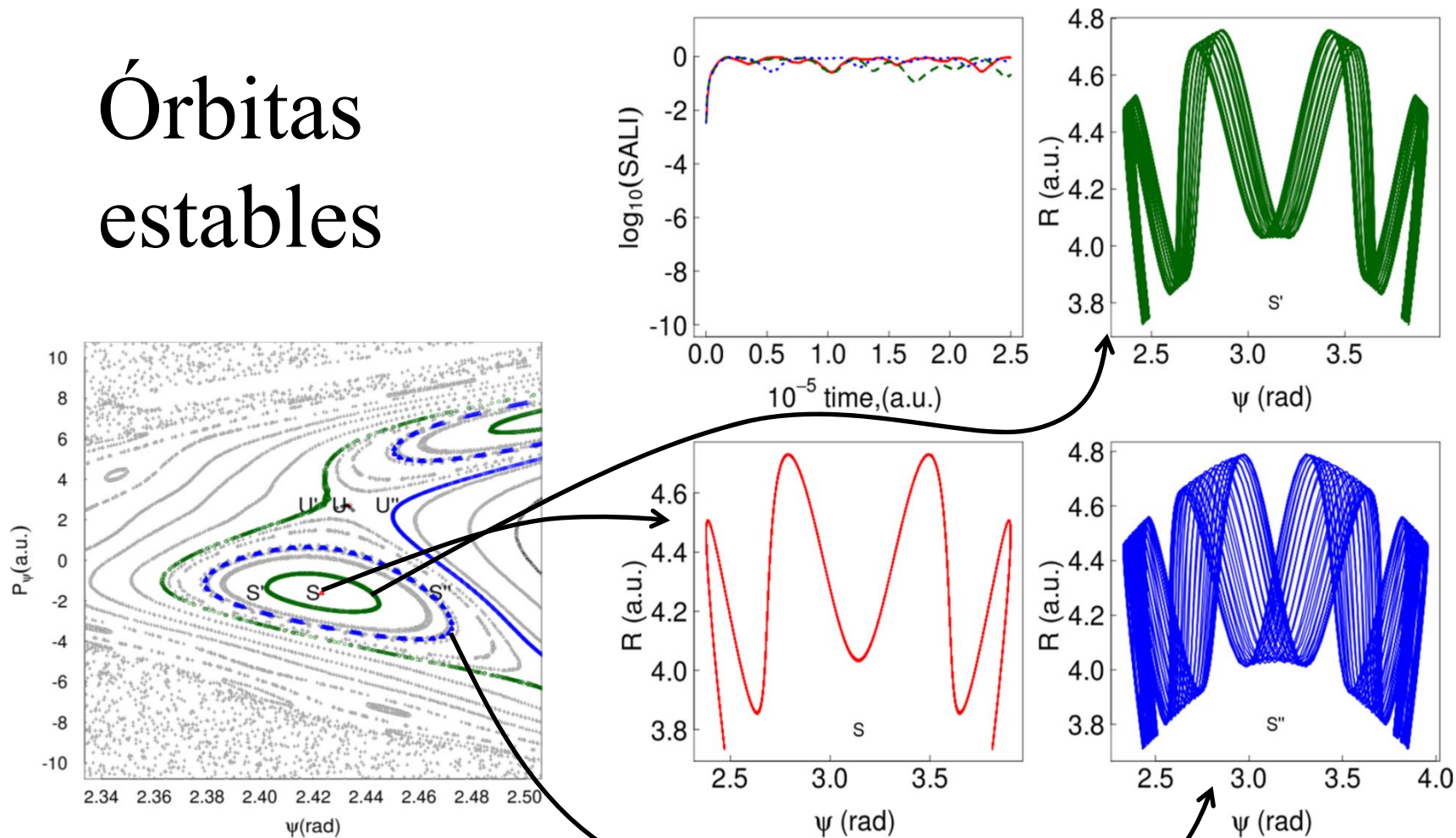
LiNC/LiCN- 2D



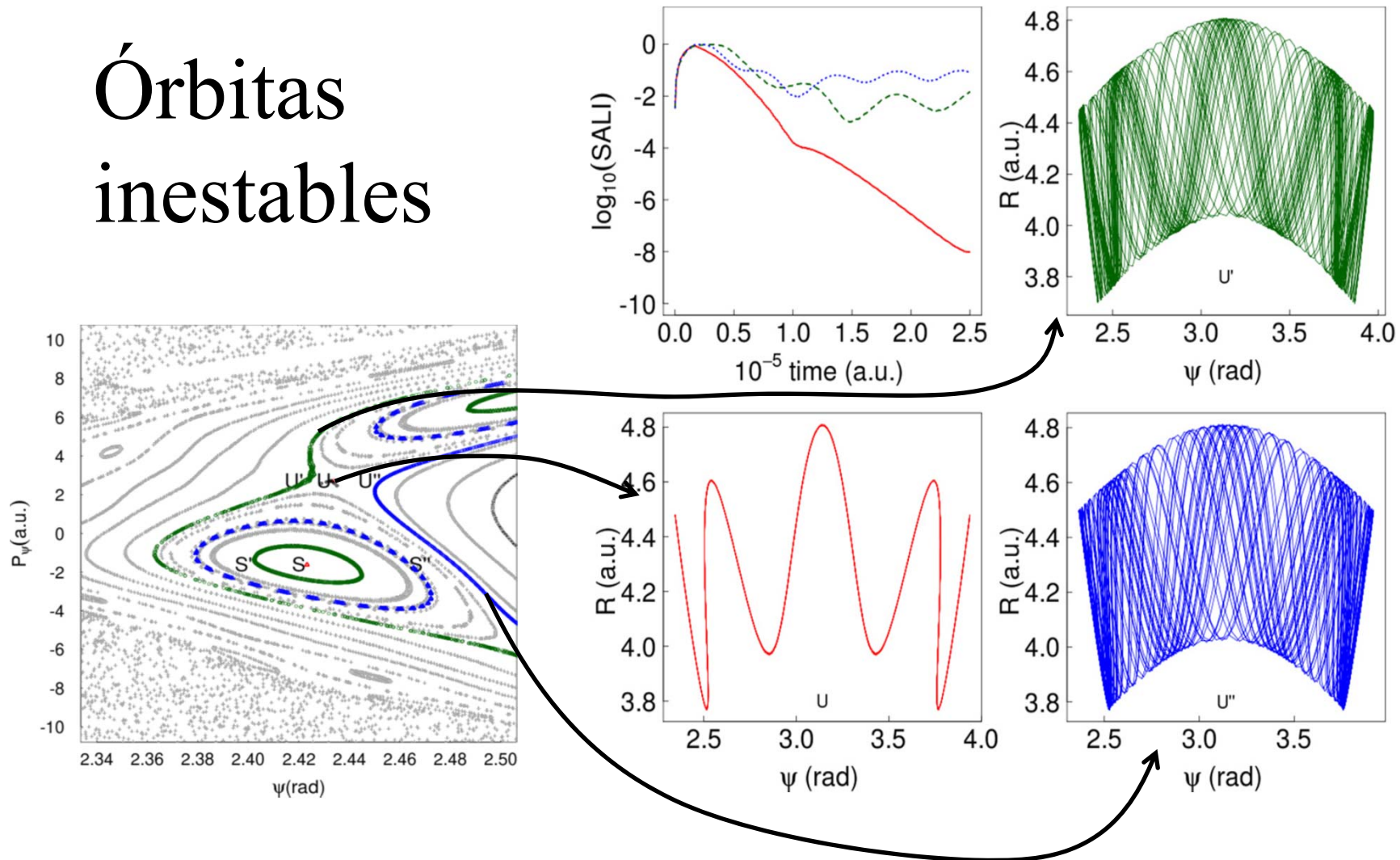
LINC/LiCN- 2D

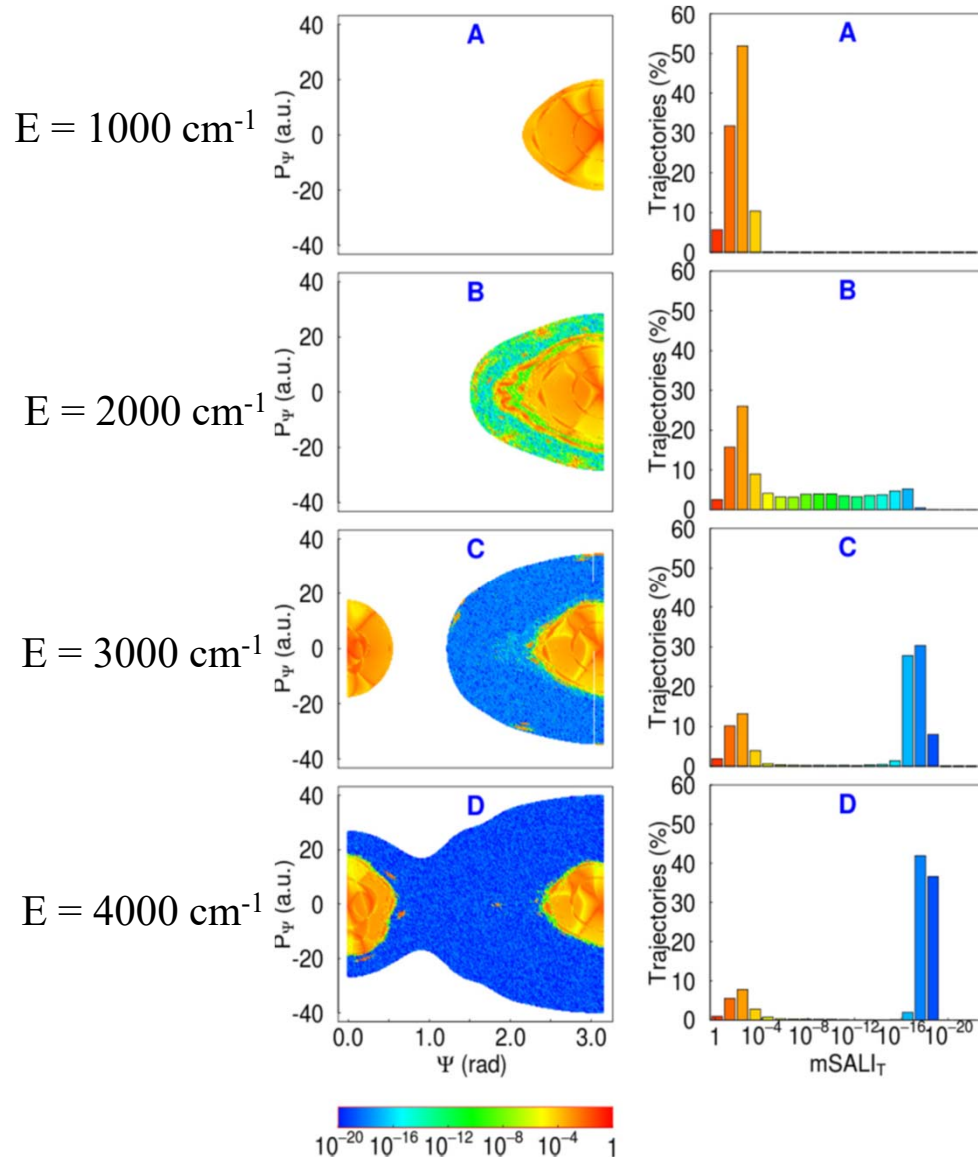


Órbitas estables



Órbitas inestables





LINC/LICN- 2D

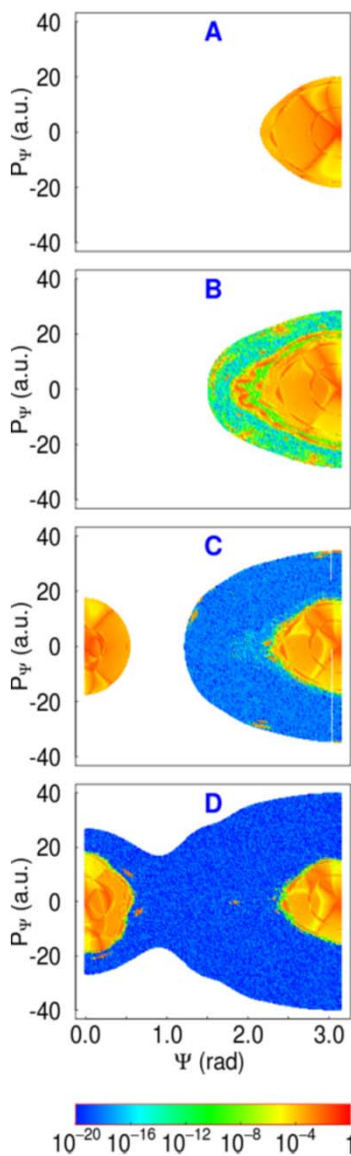
SALI MAPS

$$mSALI_T : \mathbf{R}^{2n} \rightarrow \mathbf{R}$$

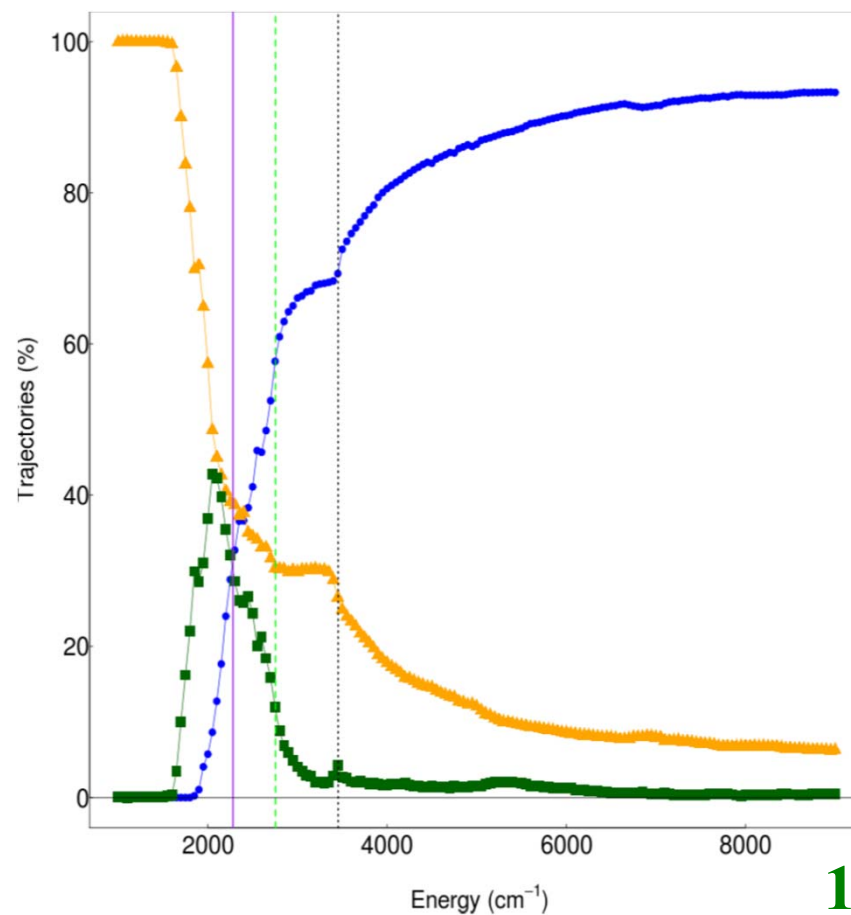
$$\text{MAP } z_0 \in \Omega_2 \rightarrow mSALI$$

Condiciones iniciales

$$\Omega_2(\psi, P_\psi) = \begin{cases} \rho & = 0, \\ P_\rho & = f(E, \psi, P_\psi, \rho) \end{cases}$$



Porcentaje de regularidad y caos



Caos fuerte
SALI < 10⁻¹⁶

Regular
SALI > 10⁻⁴
Caos débil

10⁻⁴ > SALI > 10⁻¹⁶

Geometrodinámica: reformulación del problema dinámico en términos de geometría diferencial.

Ecuaciones Euler-Lagrange

$$E_j(L) = \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}^j} \right) - \frac{\partial L}{\partial x^j} = 0$$

Ecuaciones geodésicas

$$\frac{d^2 q^i}{ds^2} + \tilde{\Gamma}_{jk}^i \frac{q^j}{ds} \frac{q^k}{ds} = 0$$

MÉTRICA JACOBI

$$g_{ij} = 2(E - V(q)) a_{ij}(q)$$

Dinámica	Geometría
Tiempo, t	Longitud de arco, s

PHYSICAL REVIEW E
 covering statistical, nonlinear, biological, and soft matter physics

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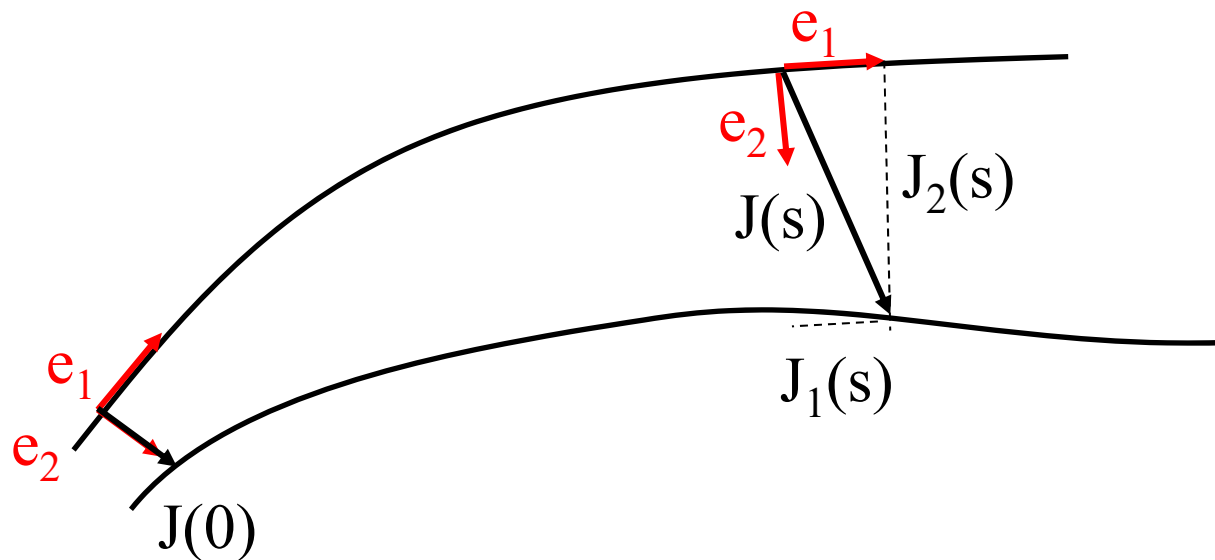
Geometrical analysis of the LiCN vibrational dynamics: A stability geometrical indicator

A. Vergel, R. M. Benito, J. C. Losada, and F. Borondo
 Phys. Rev. E **89**, 022901 – Published 3 February 2014

$\mathbf{J}(s)$ = Vector desviación geodésica

Ecuación de Jacobi-Levi-Civita

$$\frac{D^2 \mathbf{J}}{ds^2} + R[\dot{\gamma}(s), \mathbf{J}(s)] \dot{\gamma}(s) = 0$$

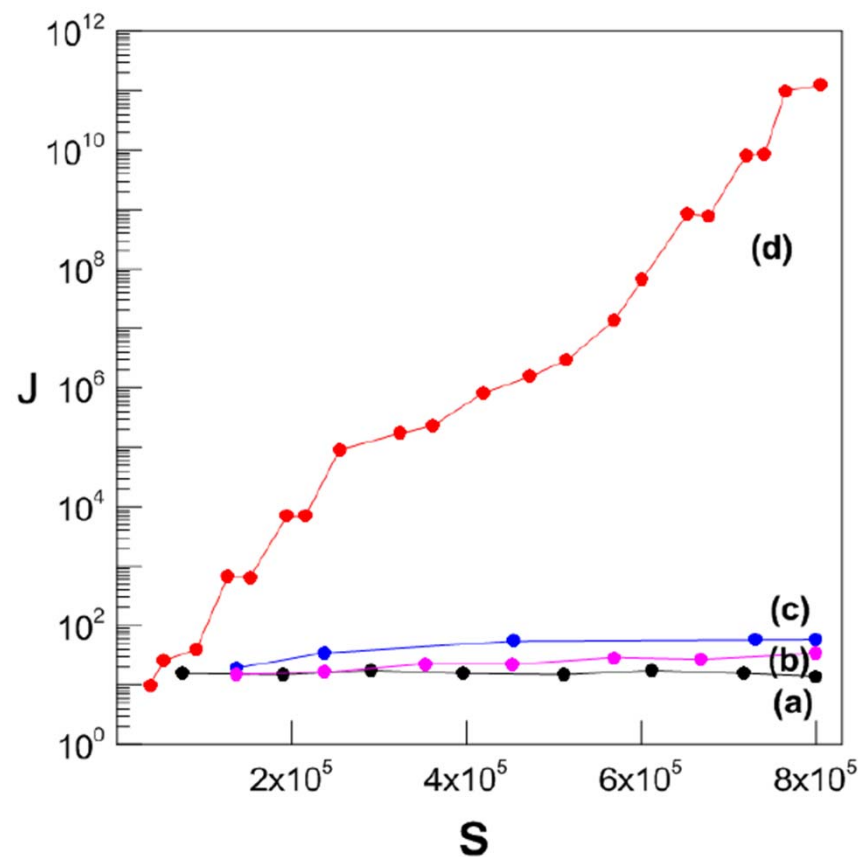
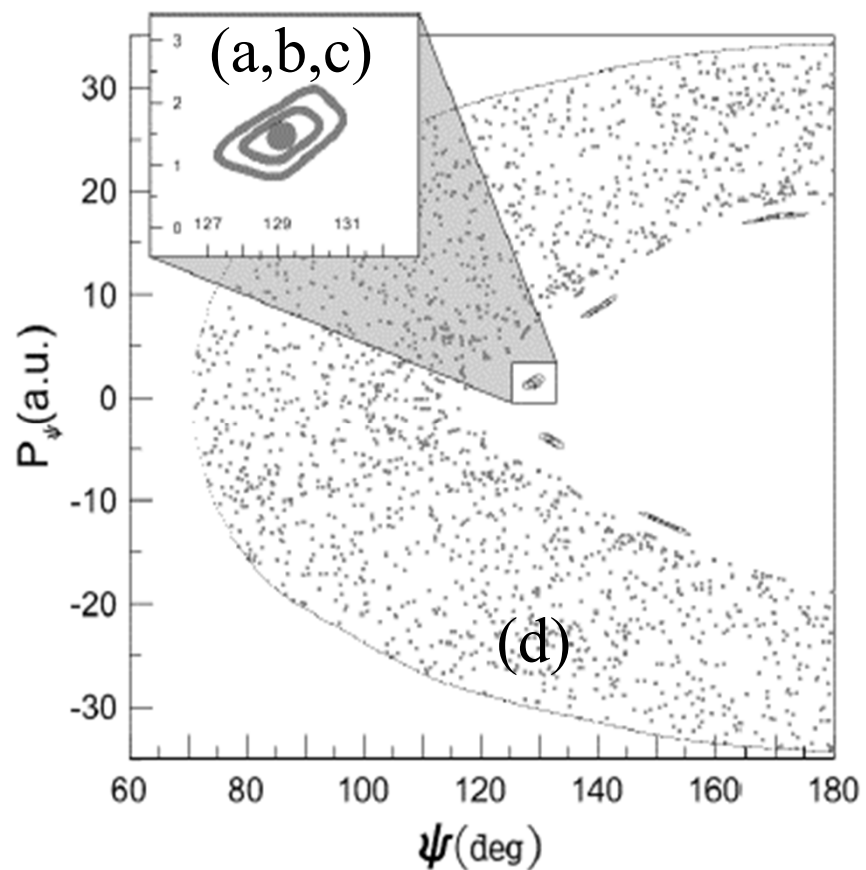


$$\frac{D^2 \mathbf{J}}{ds^2} + R[\dot{\gamma}(s), \mathbf{J}(s)] \dot{\gamma}(s) = 0$$
$$\frac{d^2 J_1}{ds^2} = 0$$
$$\frac{d^2 J_2}{ds^2} = -\frac{R(s)}{2} J_2$$

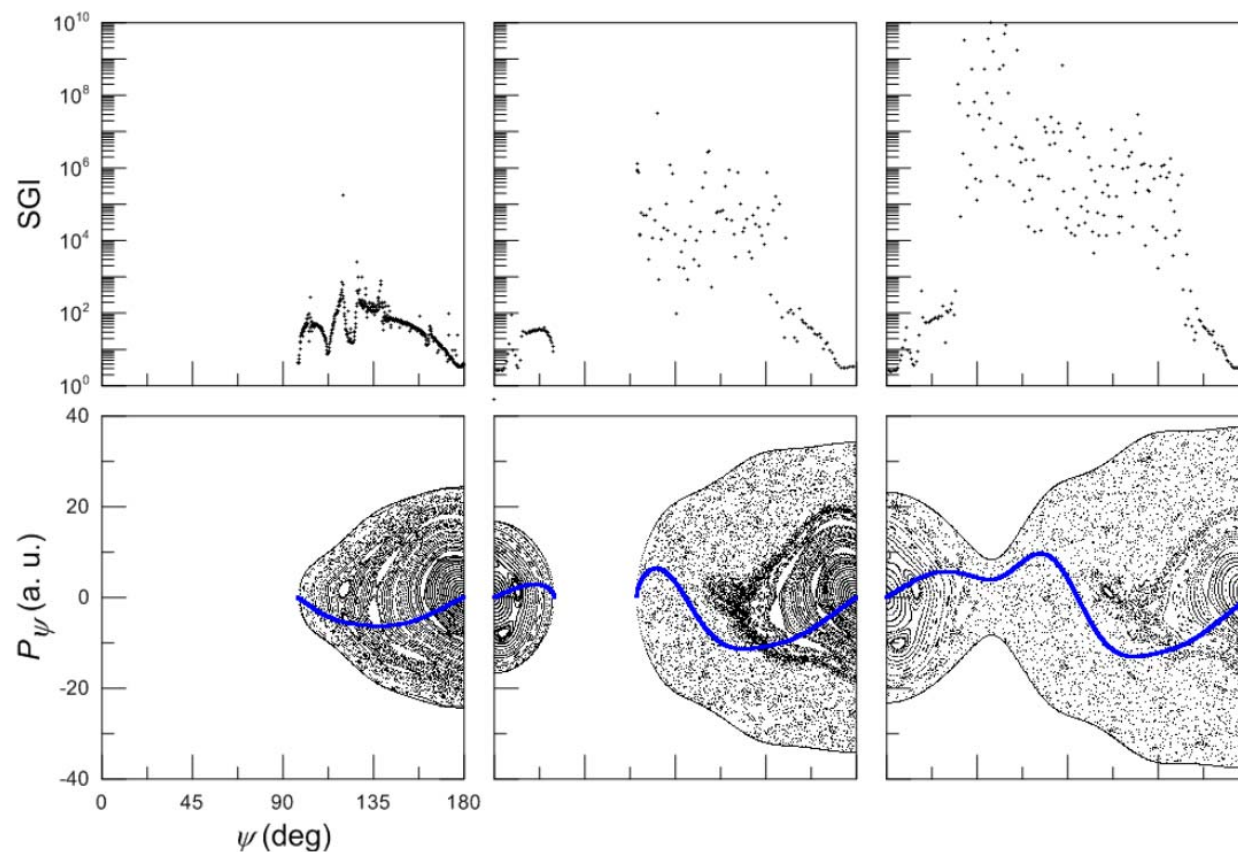
Indicador de Estabilidad para trayectorias **SGI** (*Stability Geometric Indicator*):

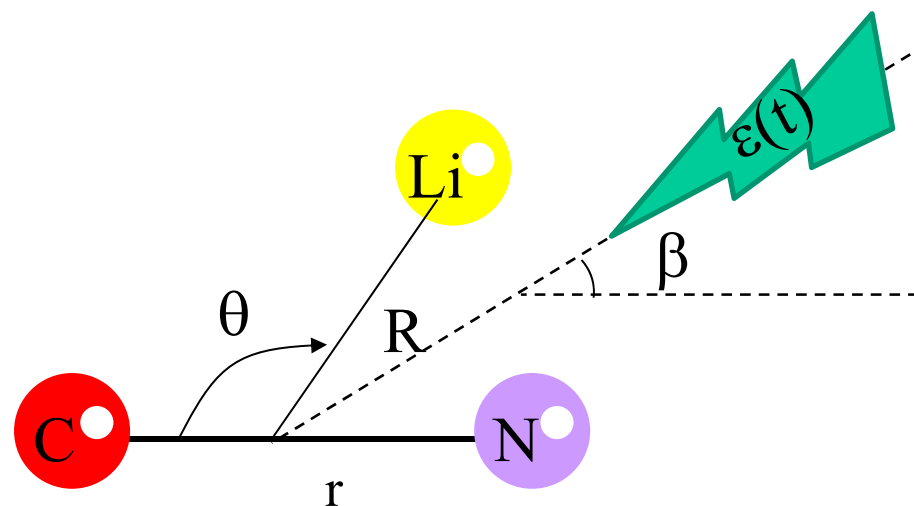
$$SGI(s, \mathbf{x}_0) = \max_{0 \leq s' \leq s} (J(s', \mathbf{x}_0))$$

Aplicación al sistema LiCN 2D



Aplicación al sistema LiCN 2D





$$H = \frac{P_R^2}{2\mu_{Li-CN}} + \left(\frac{1}{2\mu_{Li-CN}R^2} + \frac{1}{2\mu_{C-N}r^2} \right) P_\theta^2 + V(R, \theta) + H(t)$$

SISTEMA 2.5 D

De 2D a 3D: una breve historia de Dinámica No Lineal de Sistemas Moleculares



ESCUELA TÉCNICA SUPERIOR DE INGENIEROS
AGRÓNOMOS
DEPARTAMENTO DE FÍSICA Y MECÁNICA FUNDAMENTALES Y
APLICADAS A LA INGENIERÍA AGROFORESTAL



MODELIZACIÓN DE REACCIONES QUÍMICAS EN PRESENCIA DE UN CAMPO ELECTROMAGNÉTICO VARIABLE

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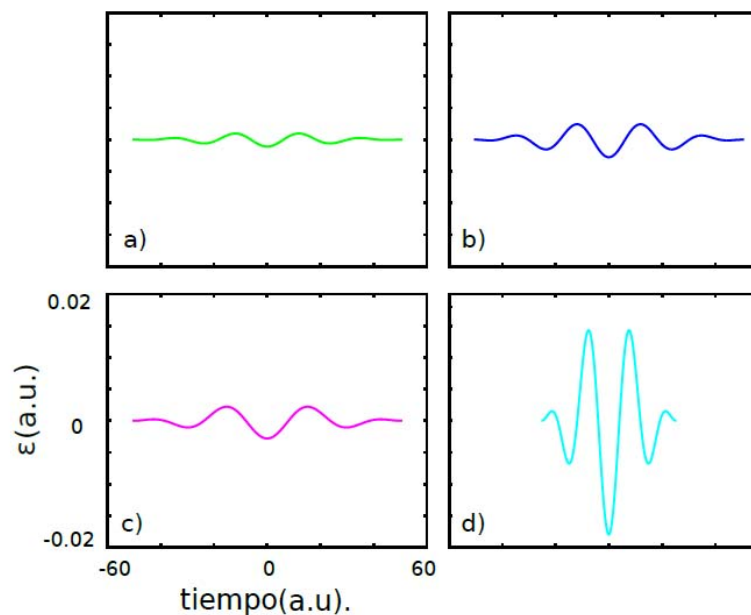
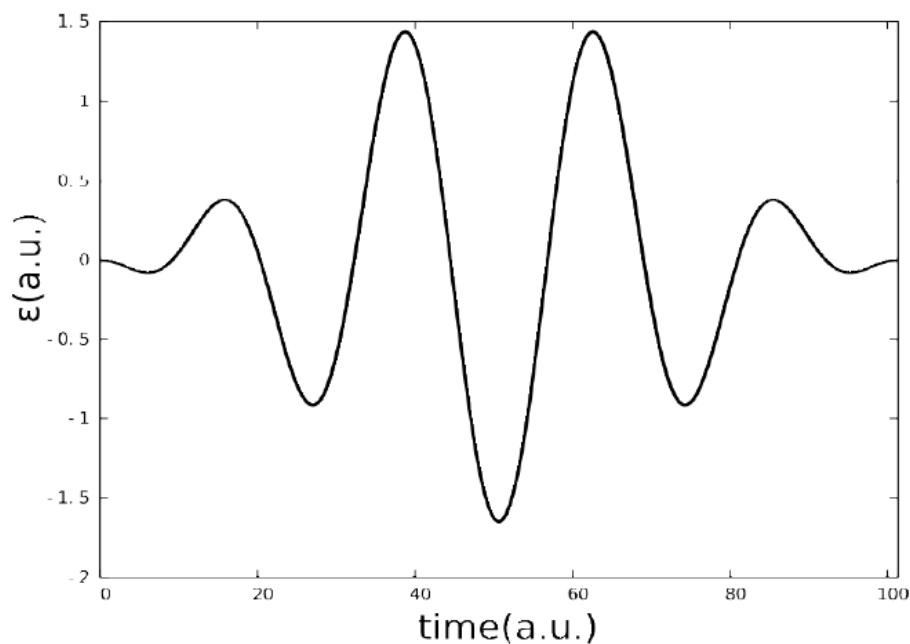
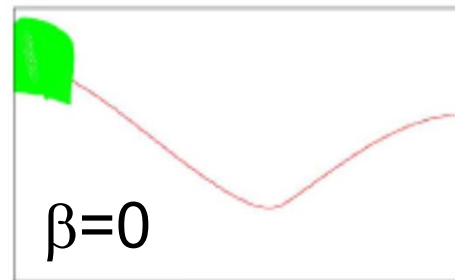
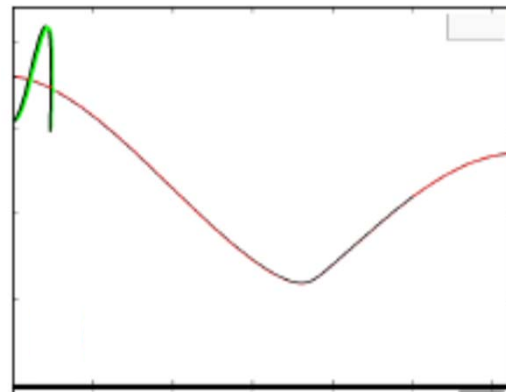


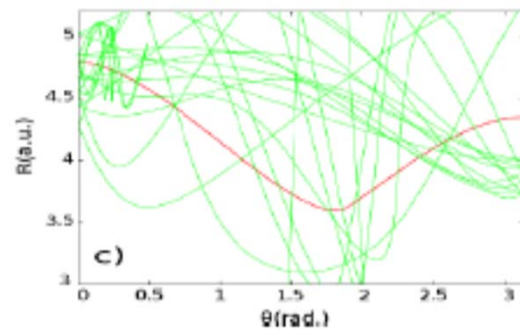
Tabla 6.2: Parámetros de los distintos pulsos ensayados y mostrados en la figura

Parámetros	Láser 0	Láser 1	Láser 2	Láser 3
Color	Verde	Azul	Magenta	Celeste
$A_0(a.u.)$	$4.434 \cdot 10^{-3}$	$1.122 \cdot 10^{-2}$	$1.496 \cdot 10^{-2}$	$4.821 \cdot 10^{-2}$
N	4	4	3	3
$T(a.u.)$	2×50.660	2×50.660	2×50.660	2×25.330

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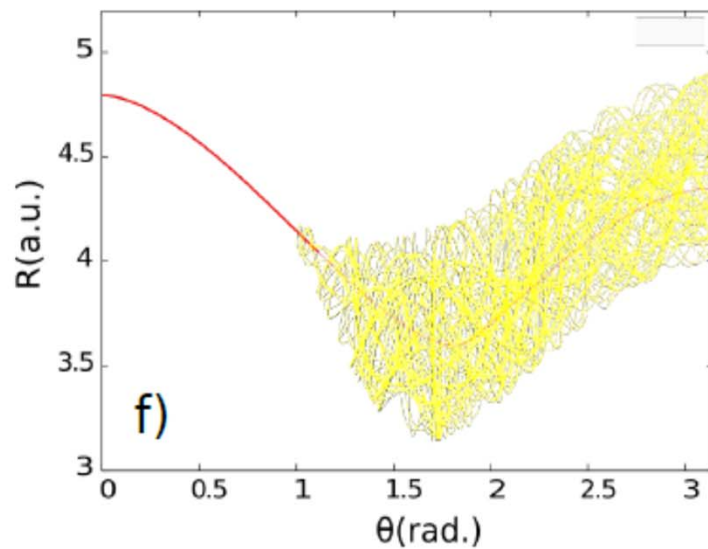
$\beta=45^\circ$



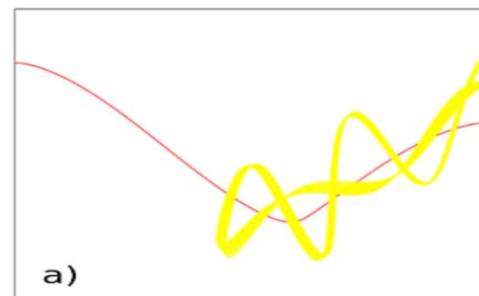
$\beta=90^\circ$



$\beta=180^\circ$



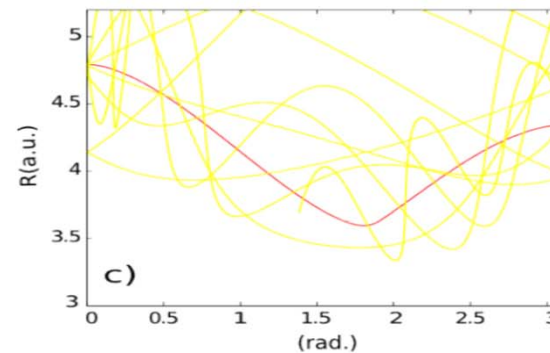
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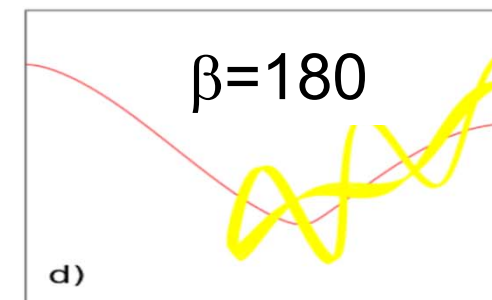
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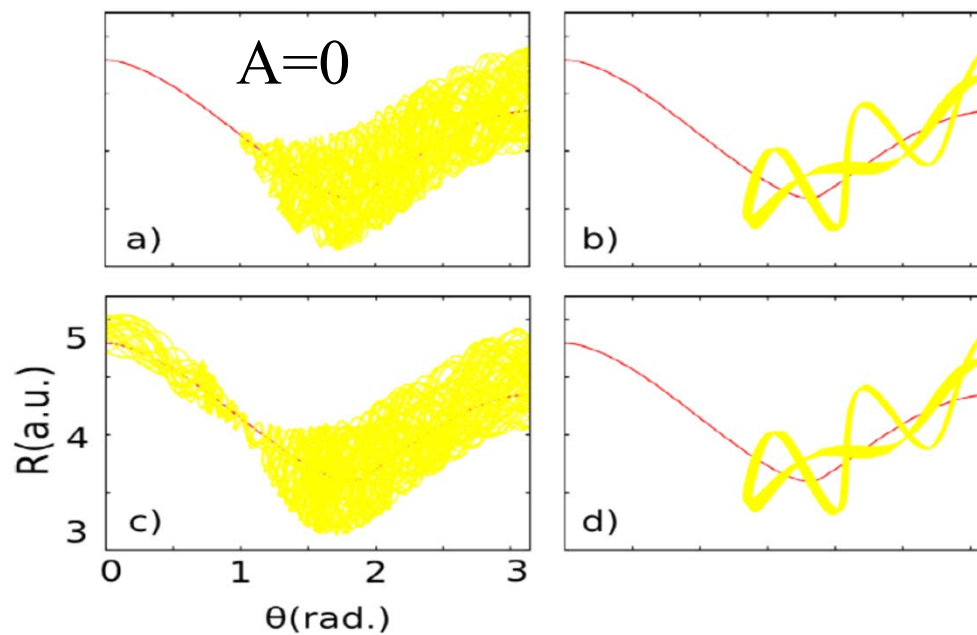
$\beta=90^\circ$



$\beta=180$

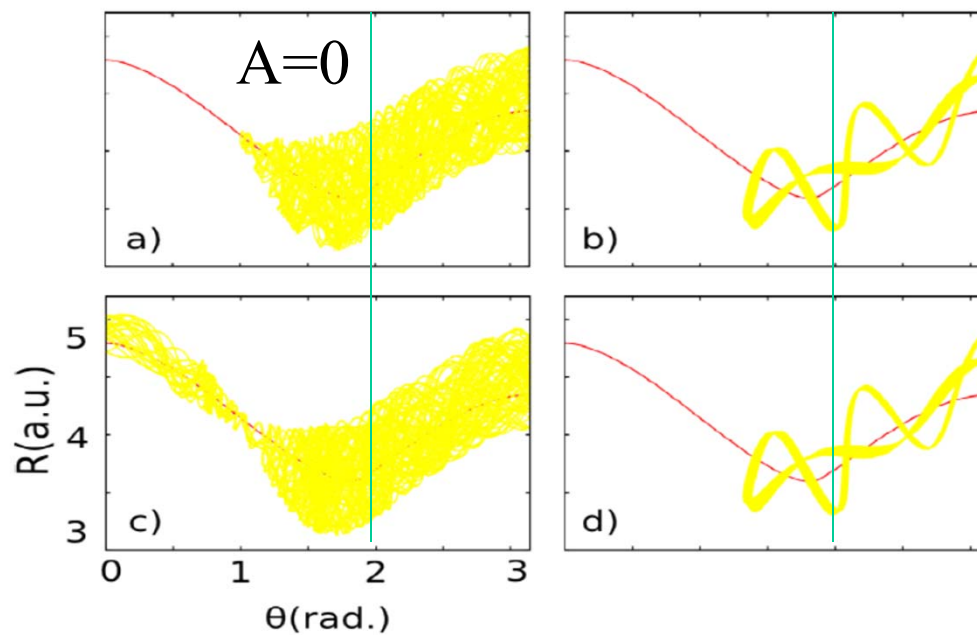


$\beta=0$

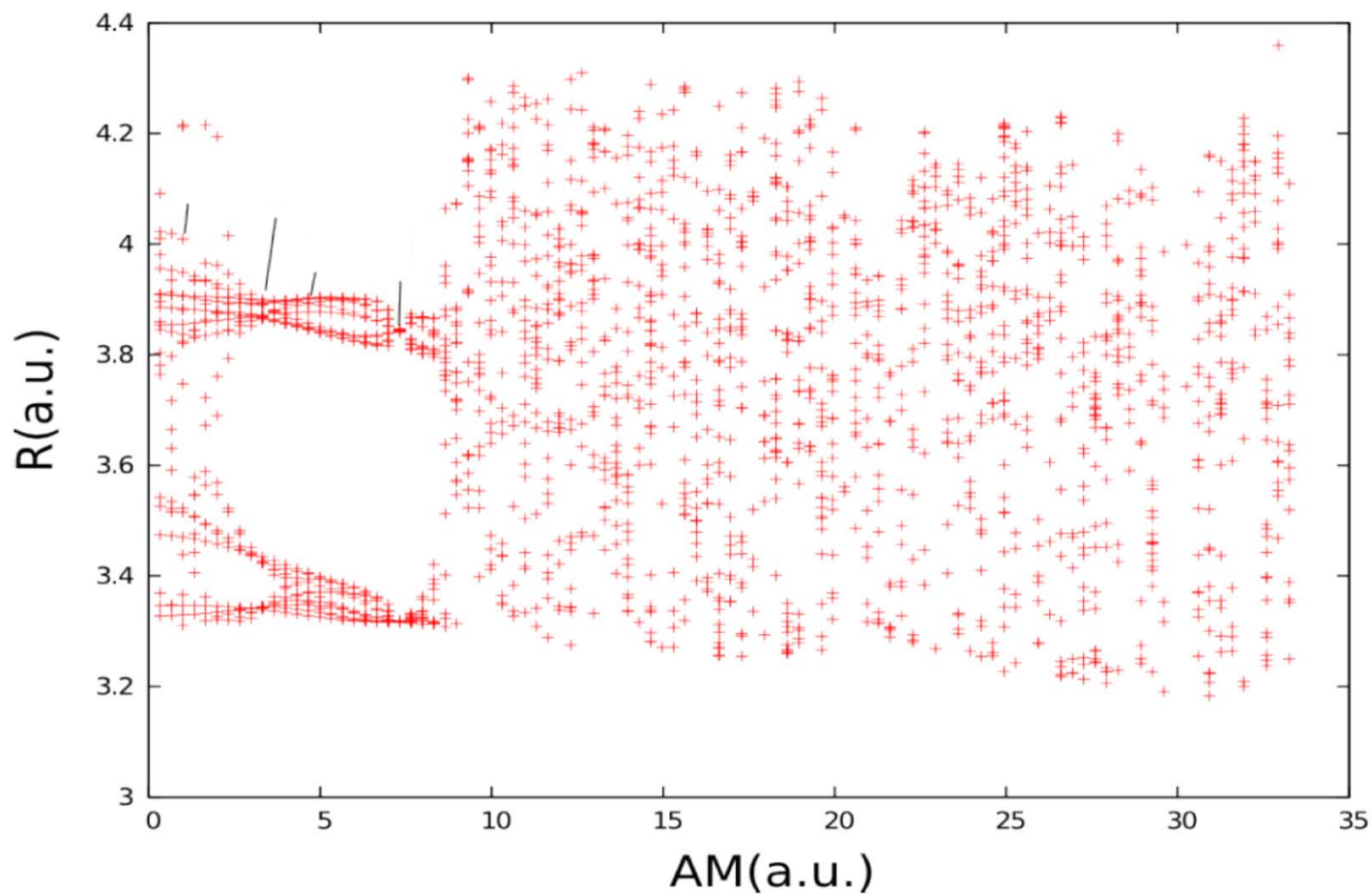


Parámetro	Láser 4	Láser 5	Láser 6
Panel	b	c	d
Energía (cm^{-1})	362133.1395	724266.2790	362133.1395
A_0 (a.u.)	6.6518	13.3036	6.6518
N	4	4	5
T (a.u.)	101.3205	101.3205	101.3205

$\beta=0$



Parámetro	Láser 4	Láser 5	Láser 6
Panel	b	c	d
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Frequency analysis of the laser driven nonlinear dynamics of HCN

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$$H(t) = H_0 + H_I = T + V + H_I(t),$$

$$T = \frac{P_1^2}{2M_{\text{CH}}} + \frac{P_1^2}{2M_{\text{CN}}} - \frac{P_1 P_2}{m_{\text{C}}},$$

$$V = D_1 (1 - e^{-\alpha_1 q_1})^2 + D_2 (1 - e^{-\alpha_2 q_2})^2$$

$$H_I = \lambda_F \mu(q_1) \cos \omega_F t$$

EN AUSENCIA DE LASER

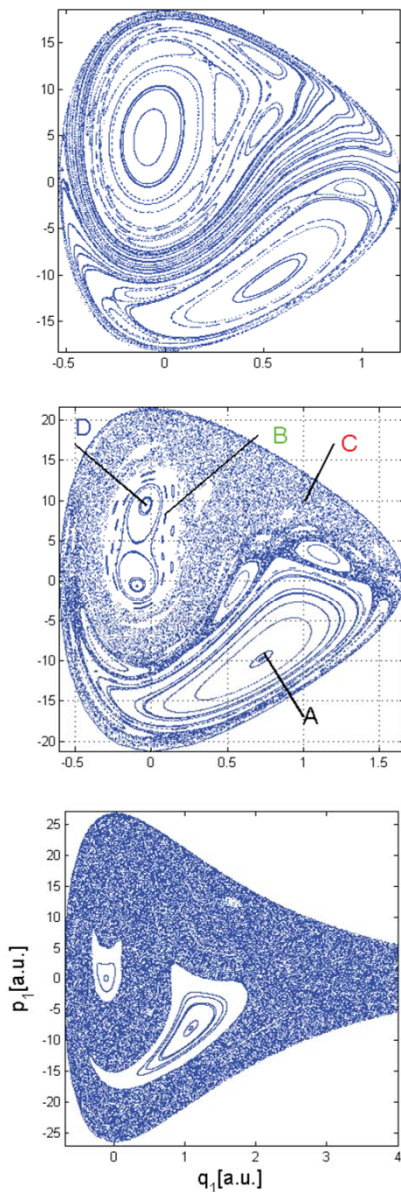


Figure 3. Composite Poincaré surfaces of section for the HCN molecule without interaction with the laser at $E = 0.1$ (top), 0.135 (middle), and 0.21 (bottom), corresponding to intersections with the plane $q_2 = 0$ with $P_2 > 0$. Four representative trajectories, marked A–D in the middle panel, are analyzed in the text. (Atomic units are used in all figures of this paper.)

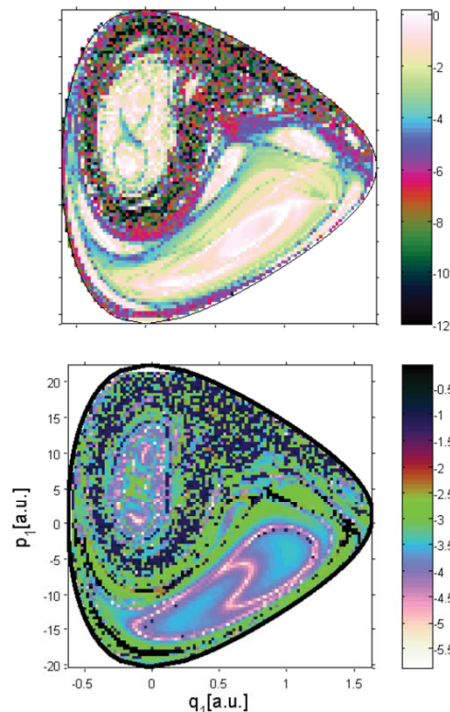


Figure 5. SALI (top) and diffusion coefficient (bottom) colored PSOS maps for the HCN molecule without interaction with the laser, for $E = 0.135$. Values are shown using the color code given on a logarithmic scale at the right of the plots.

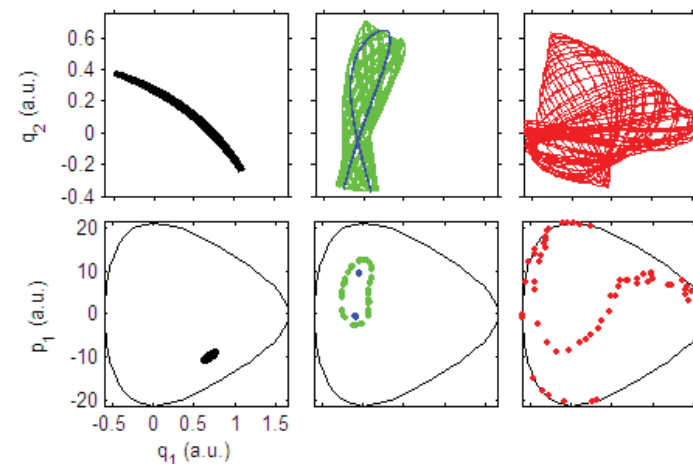


Figure 4. Trajectories A (left tier), B and C (middle tier), and D (right tier) for the HCN molecule without interaction with the laser marked in Fig. ???. The top row plots show the orbits in configuration space, while those at the bottom corresponds to Poincaré surfaces of sections.

**DOS RESONANCIAS
 IMPORTANTES
 1:1 and 3:2**

$$\omega^* = \omega_{[1,1]}$$

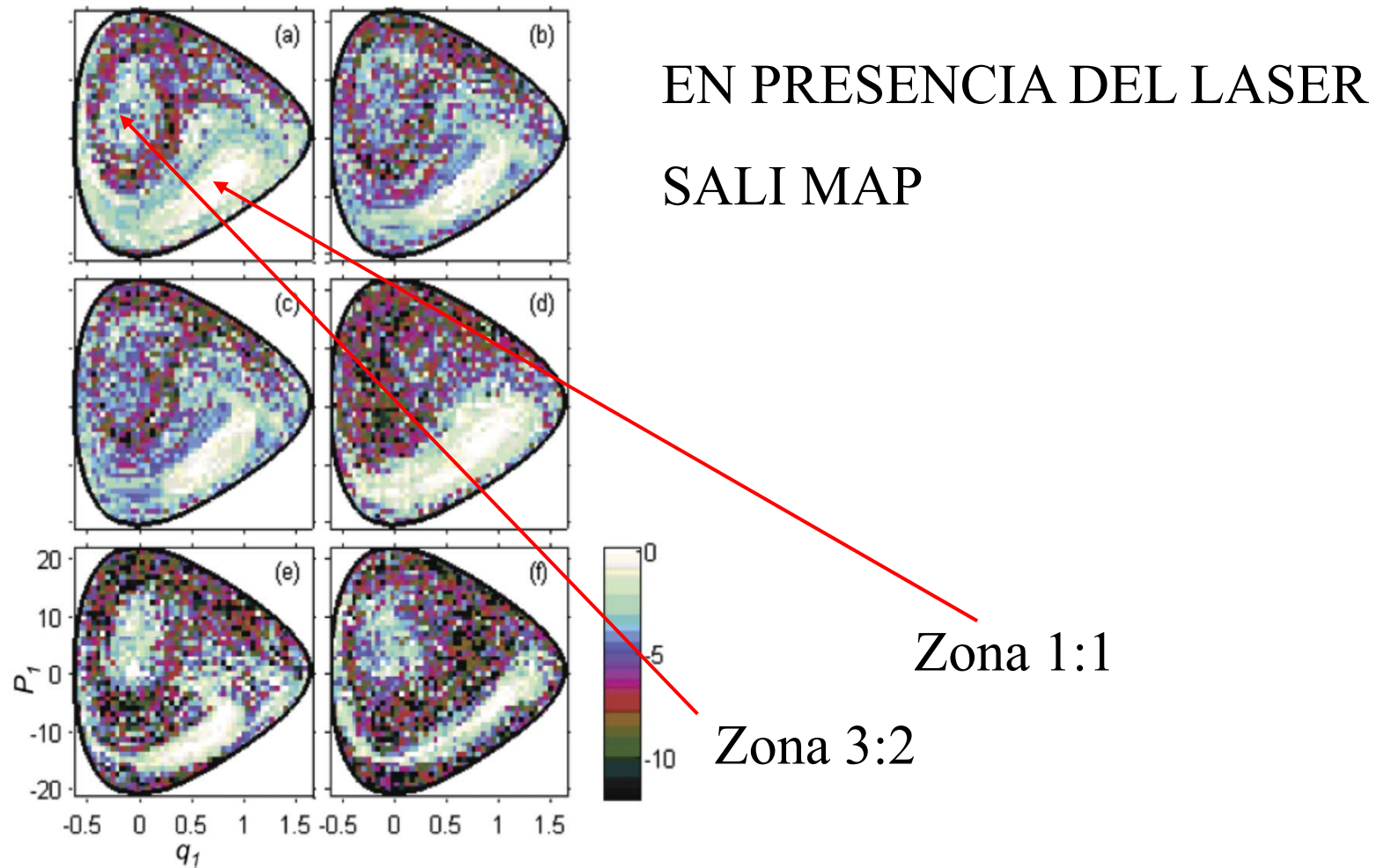
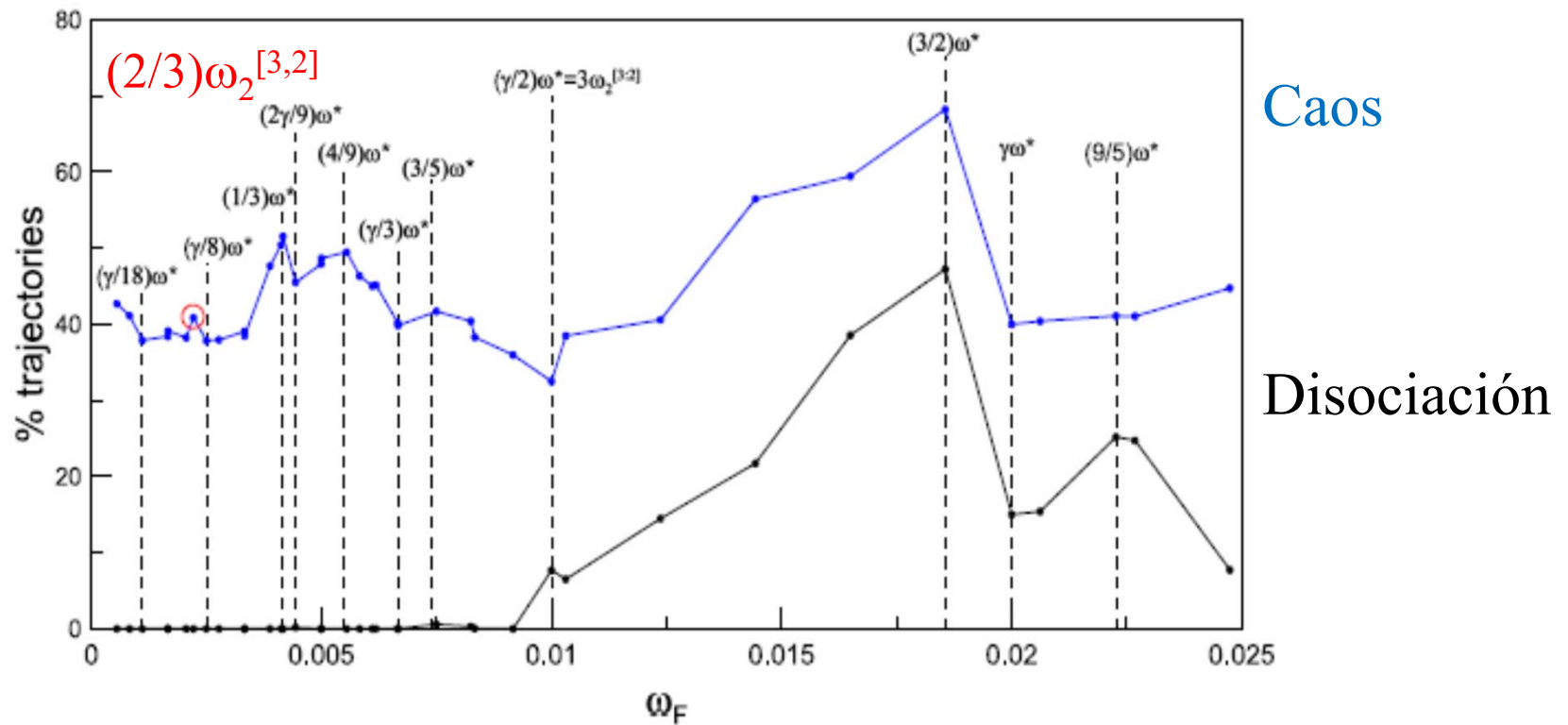
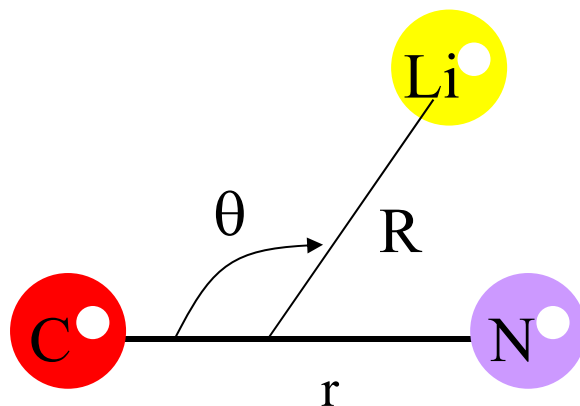


FIG. 6. SALI colored Poincaré surface of section map, as defined in Subsection III B, for HCN in the presence of a laser with the following values of the frequency: $\omega_F = 0.003\,333$ (a), $0.004\,123$ (b), $0.009\,278$ (c), $0.010\,000$ (d), $0.014\,430$ (e), and $0.018\,556$ (f), respectively. In all cases the initial energy without the interaction with the laser is taken equal to $E_0 = 0.135$.





$$H = \frac{P_R^2}{2\mu_{Li-CN}} + \left(\frac{1}{2\mu_{Li-CN}R^2} + \frac{1}{2\mu_{C-N}r^2} \right) P_\theta^2 + V(R, \theta) +$$

$$+ \frac{P_r^2}{2\mu_{C-N}} + M(r)$$

SALI MAPS

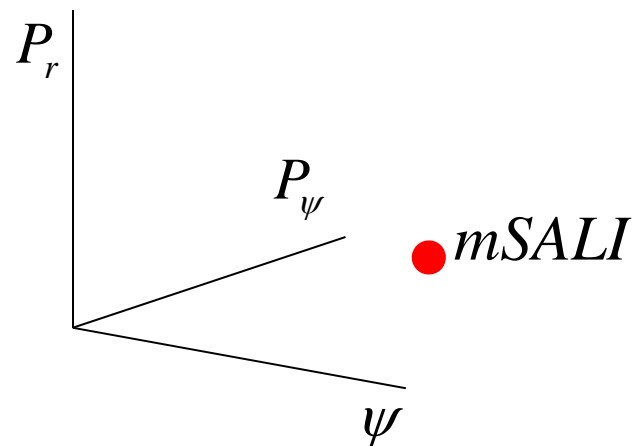
$$mSALI_T : \mathbf{R}^{2n} \rightarrow \mathbf{R}$$

$$\text{MAP } z_0 \in \Omega_3 \rightarrow mSALI$$

Initial Conditions

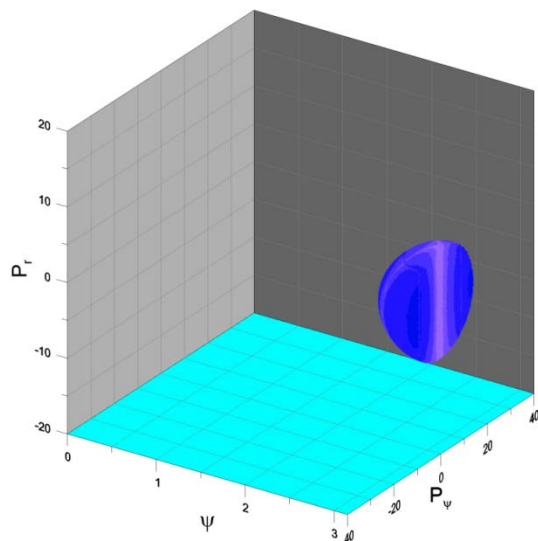
$$\Omega_3(\psi, P_\psi, P_r) = \begin{cases} r = r_e \\ R = R_e(\theta) \Rightarrow \rho = 0 \\ P_\rho = f(E, \psi, P_\psi, P_r, r, \rho) \end{cases}$$

4D- visualization

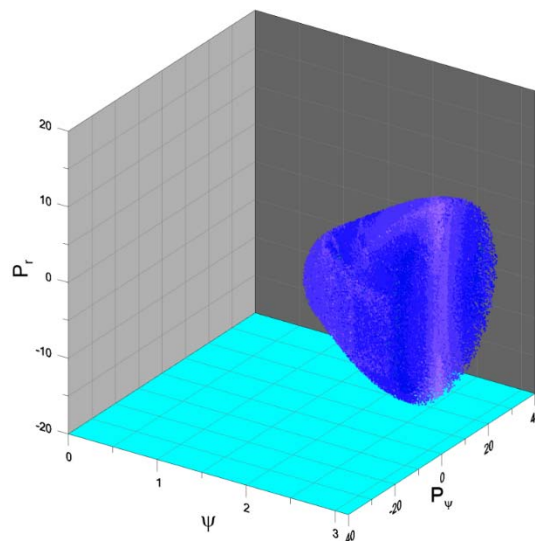


LiNC/LiCN- 3D

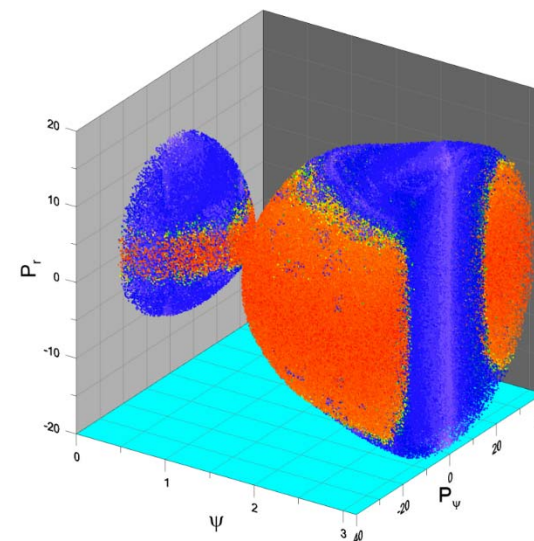
$E = 512 \text{ cm}^{-1}$



$E = 1510.5 \text{ cm}^{-1}$

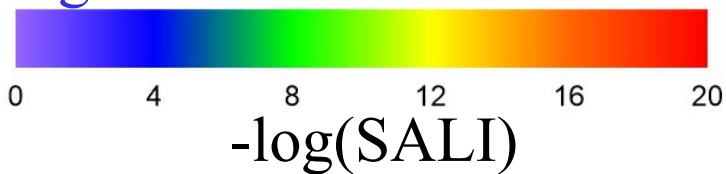


$E = 3500 \text{ cm}^{-1}$



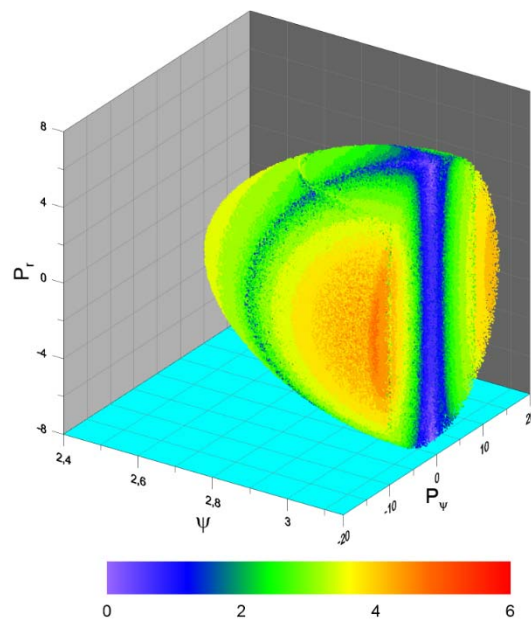
Regular

Chaos



LiNC/LiCN- 3D

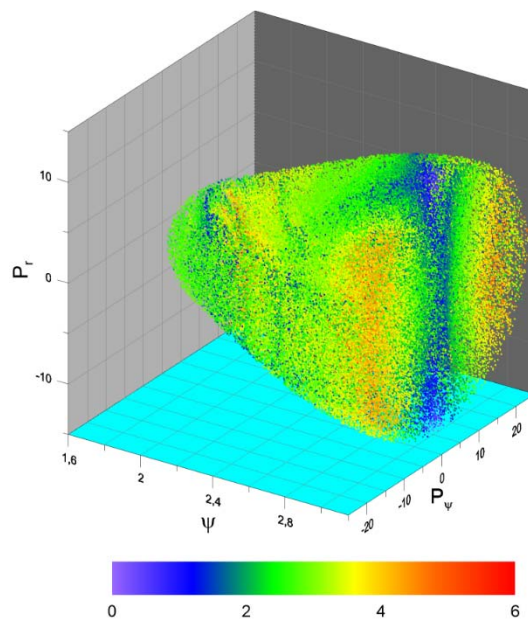
$E= 512 \text{ cm}^{-1}$



$-\log(\text{SALI})$

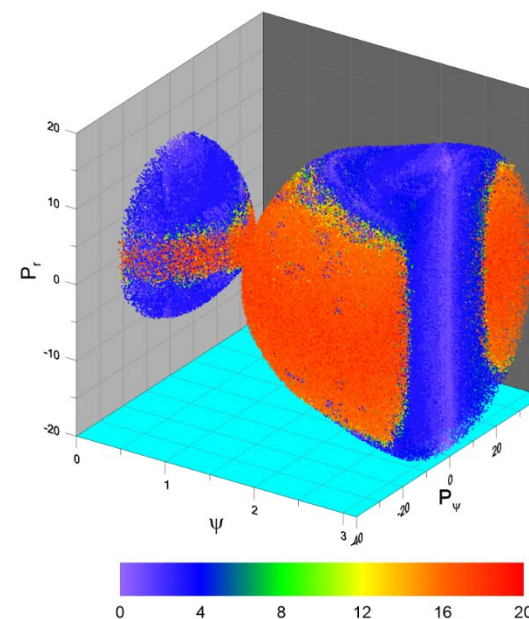
Regular

$E= 1510.5 \text{ cm}^{-1}$



$-\log(\text{SALI})$

$E= 3500 \text{ cm}^{-1}$

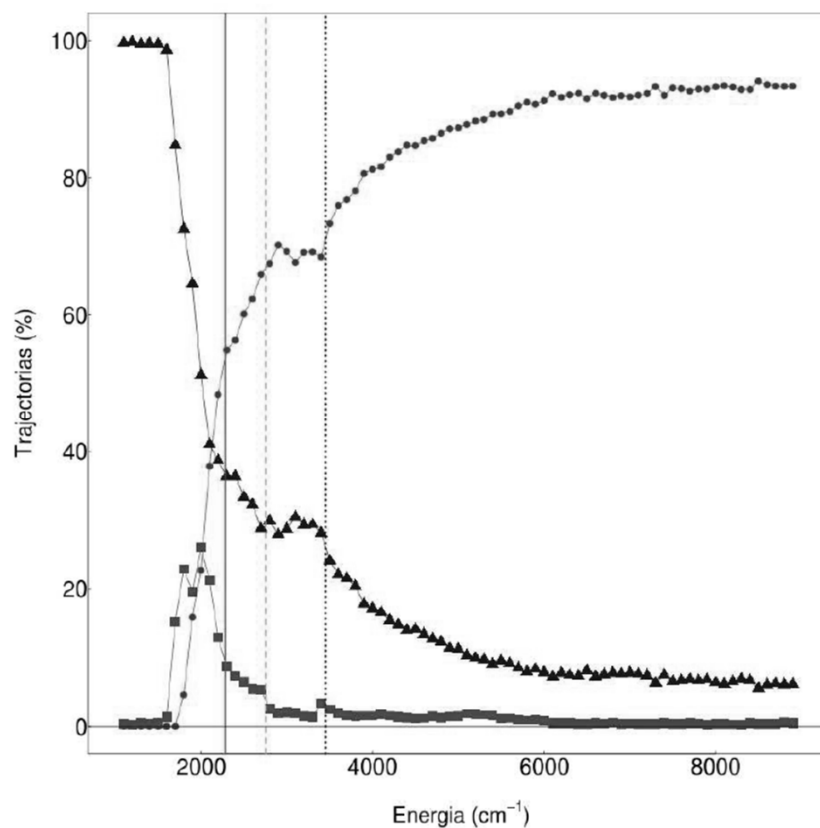


$-\log(\text{SALI})$

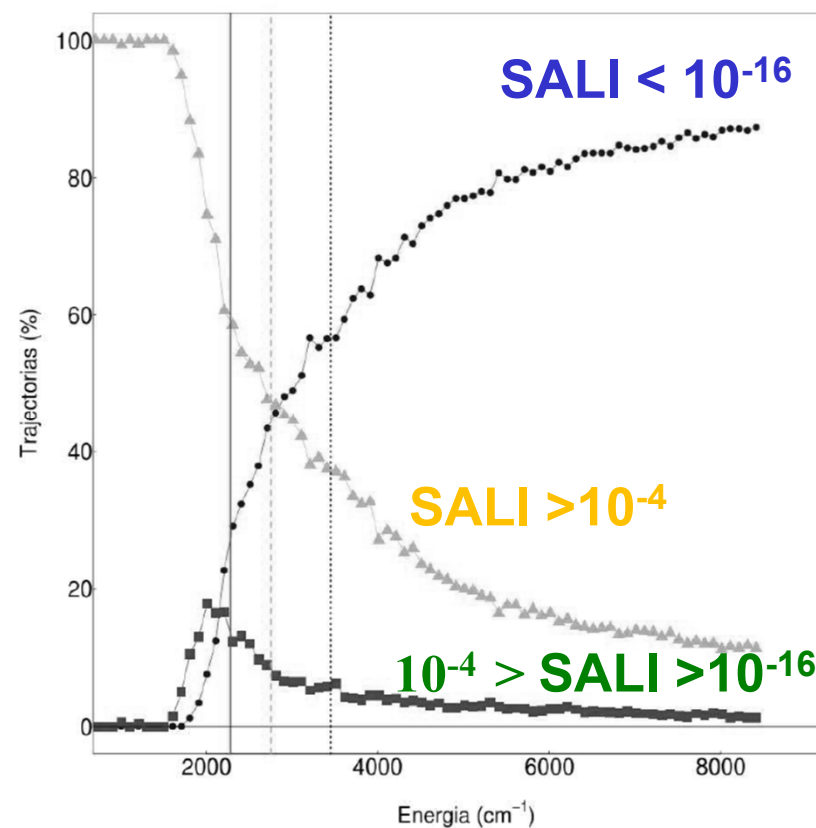
Chaos

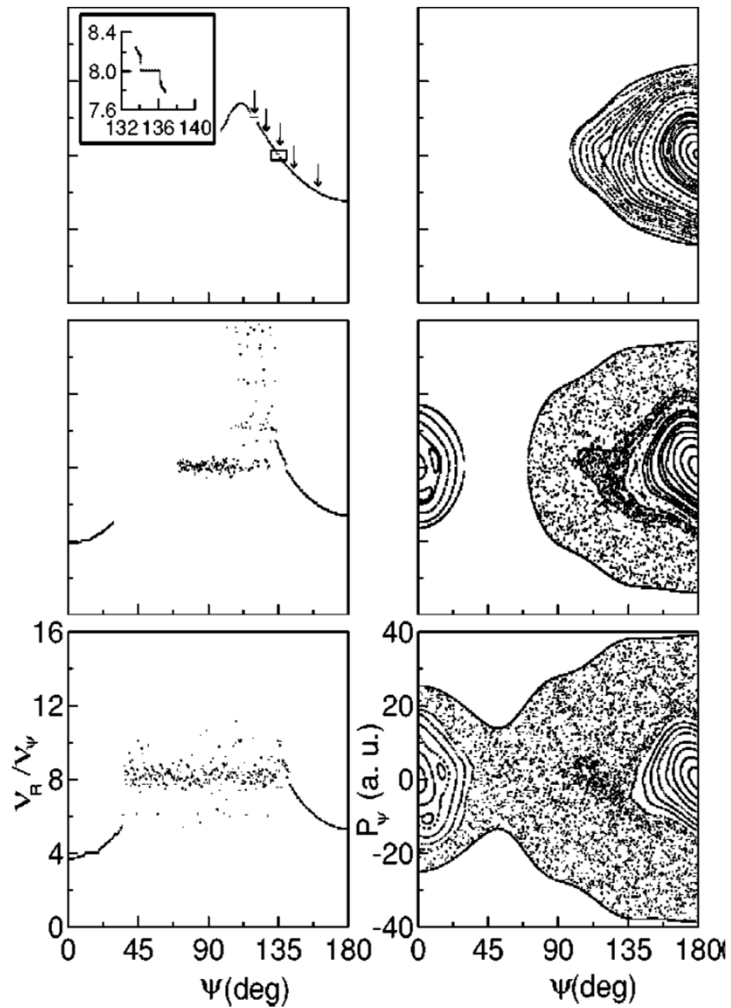
Porcentaje de regularidad y caos


2D

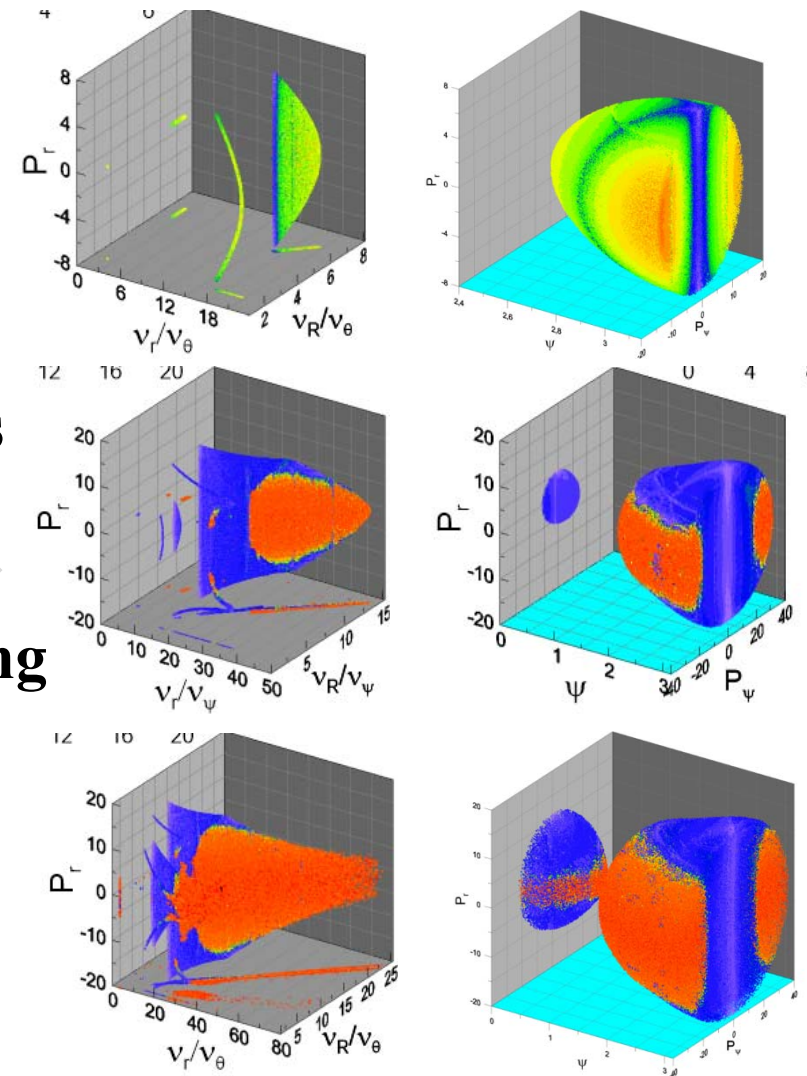


3D





20 years

 is nothing





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No Lineal de Sistemas Moleculares*

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