Multifractal Analysis of the Frequency Map in a Chaotic Molecular System

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Abstract: - Relations between the frequency map of a generic Hamiltonian model, describing the vibrational dynamics of the LiNC/LiCN molecular system, and its chaotic behavior are discussed. The scaling structure of the local frequency map is studied based on the multifractal analysis. This approach allows different behaviors to be recognized as well as to study the evolution of the molecular system at different vibrational energies.

Key-Words: - multifractal, scaling structure, frequency map, local frequency analysis, chaos, molecular system

1 Introduction

If \( H_0 \) is a Hamiltonian system with \( N \) degrees of freedom, the equations of motion, expressed in action-angle variables, are given by:

\[
\dot{I}_j = \frac{\partial H_0(I)}{\partial \theta_j} = 0, \quad \dot{\theta}_j = \frac{\partial H_0(I)}{\partial I_j} = v_j(I) \quad (1)
\]

The trajectories in phase space lie on the surface of tori, which are the result of a product of circles with a constant radius \( I_j = I_j(0) \) and described with a constant velocity \( v_j \).

According with KAM theorem, Hamiltonian systems slightly perturbed keep part of the tori undestroyed. The family of these persistent tori is parameterized by a Cantor set of frequency vectors \( \nu = \{\nu_1, \nu_2, ..., \nu_n\} \). In the hollows of this set is where the chaotic behavior is observed.

In systems where \( N=2 \), the quasiperiodic trajectories that persist involve the tori surface (a 2D surface) in a 3D space. These are barriers for the rest of the trajectories. Also the nonresonant tori which are destroyed turn into fractal objects called cantori and constitute partial barriers for the flux of the trajectories in phase space.

The frequency map (FM) might be also viewed as a measure which represents the ensemble of multiple interrelated processes of tori degradation turning into cantori [1]. This measure (FM) may display a selfsimilarity referred to as multifractal [2]. In this work FM is studied in terms of the percentage of frequency distributed in different initial conditions (\( \psi \) angle) obtained from frequency analysis. Thus, one value may be taken as the fraction FM, \( p_i \), in an angle class “i”. The support of this measure is the set of real numbers corresponding to \( \psi \) values from \( \psi_i \) to \( \psi_f \) degrees. Thus, \( p_i \) can be interpreted as the probability of finding frequencies of a certain value with \( \psi \) interval “i” and it follows that \( p(\psi_i, \psi_f)=1 \) (or 100%). However \( p \) may be spread over the interval \( \psi_i, \psi_f \) in such way that the concentration of frequencies varies widely.

With this definition of a probability measure, \( p_i \), the idea of fractal dimension is extended by considering the various moments, \( q \), of the measure normalized by their sum:

\[
\mu_i(q,\delta) = \frac{p_i^q}{\mu(\delta)} = \frac{p_i^q}{\sum_{i=1}^n p_i^q} \quad (2)
\]

Where \( n(\delta) \) is the number of subintervals of size \( \delta \) in largest interval \( \psi_i, \psi_f \), \( \mu_i \) is the percentage of FM in the subinterval \( i \) and \( q \) is the weight or moment of the measure. The sum in the denominator of Eq. 2, \( \mu(q, \delta) \), is dominated by the highest values of \( p_i \) when \( \delta \to 0 \) if \( q>0 \) and by the smallest values of \( p_i \) if \( q<0 \).
A log-log plot of a selfsimilar measure, \( \mu(q, \delta) \), vs. \( \delta \) at various values for \( q \) will give:

\[
\mu(q, \delta) \sim \delta^{-\tau(q)}
\]

where \( \tau(q) \) is called the qth mass exponent [4]. If Eq. 3 is compared with the classical relation

\[
N(\delta) \sim \delta^{-D}
\]

\( \tau(q) \) is seen to play the role of a fractal dimension but it is not constant over all length scales. Instead, if \( \tau(q) \) is plotted vs. \( q \), a multifractal measure will yield a convex function [3].

Results can be expressed in terms of the measure's multifractal spectrum, \( f(\alpha) \), which is defined by a Legendre transformation as follows:

\[
\alpha(q) = -\frac{d}{dq} \tau(q)
\]

\[
f(\alpha(q)) = q\alpha(q) + \tau(q)
\]

where \( \alpha \) is the Lipschitz-Hölder exponent which characterizes the average strength of singularity in the measure \( \mu \) [2]. The quantity \( f(\alpha) \) may be interpreted as the fractal dimension of the subset of the interval \([\psi_i, \psi_j] \) that dominates the sum in Eq. 2 for different weights \( q \) having the same Lipschitz-Hölder exponent \( (\alpha) \) [4].

The \( f(\alpha) \) curve typically has a parabolic shape. Several meaningful parameter can be obtained from the spectrum. Two of them are \( \alpha_{\text{max}} \) and \( \alpha_{\text{min}} \) which give the amplitude of the convex function \( (f(\alpha)) \), defined for the case when \( f(\alpha) = 0 \), as \( \alpha_{\text{max}} - \alpha_{\text{min}} \).

2 System and Computational Method

2.1 The LiCN Molecular System

The system that we study in this paper is a two degrees of freedom model for the LiNC/LiCN molecule, in which the C-N bond frequency is very high, and the corresponding motion separates easily from the rest of the molecular vibrations. The classical vibrational Hamiltonian \((J=0)\) is given by:

\[
H=\frac{p_R^2}{2\mu_{\text{Li-CN}}} + \frac{1}{2\mu_{\text{Li-CN}}} \sum R^2 + \frac{1}{\mu_{\text{C-N}}} \sum \theta^2 + V(R, \theta)
\]

(7)

Where \( R \) is the distance from the center of mass of the CN fragment to the Li atom, \( \theta \) is the angle between the N-C and R vectors, and \( p_R \) and \( p_\theta \) are the corresponding conjugate momenta.

The classical dynamics of this system is followed by classical trajectory calculation, using a Gear algorithm for the numerical integration of Hamilton’s equations of motion corresponding to Eq 7.

2.2 Frequency Map

The method applied in this case is based that, under certain conditions of \( H_0 \) verified in almost of the physic systems, the relation \( \mathbf{v} = f(I) \) given in (1) can be inverted. Then, \( I = F(\mathbf{v}) \) and the frequency map [5] [6] is given by:

\[
F_{\theta_i} : B^n \longrightarrow \mathbb{R}^n
\]

\( (l) \longrightarrow (v) \)

(8)

where \( B^n \) is a domain of \( \mathbb{R}^n \), which depends on the system energy. \( \theta_i \) indicates that all the values of the variables \( \theta = \theta(0) \) are fixed on the tori of radio \( I_j \). As the energy is preserved, one of the action variables can be expressed in function of the rest of them, \( I_n = f \left( I_1, I_2, ..., I_{n-1}, I_n \right) \), and then it is possible to build the frequency map as:

\[
F_{\theta_i} : B^{n-1} \longrightarrow \mathbb{R}^{n-1}
\]

\( (l)_{n-1} \longrightarrow \left( \frac{\mathbf{v}_1}{\mathbf{v}_2}, \frac{\mathbf{v}_3}{\mathbf{v}_4}, ..., \frac{\mathbf{v}_{n-1}}{\mathbf{v}_n} \right) \)

(9)

If \( A \) is a subset of \( B^{n-1} \), with values from \( (l)_{n-1} \) such as \( (l)_{n-1}, I_{n-1}, \theta_{n-1} \) belongs to a KAM tori of dimension \( n \). In other words, \( A \) is a subset of the space where the trajectory is regular, then it can be proved that:

- \( F_{\theta_i} \) on \( A \) is constant in time
- \( F_{\theta_i} \) on \( A \) is regular,

therefore, if the frequency map is extended to all the subset \( B^{n-1} \), when \( F_{\theta_i} \) is not regular the corresponding KAM tori have been destroyed.

The analysis of the frequency map consist to obtain this map searching for numerical solutions with quasi-periodic approaches in a finite interval of time, \( T \). The numerical method to calculate the fundamental frequencies is done by a searching in a frequencies database, which depends on the trajectory, the one that maximize in each term the contribution to the whole function. Following this method the precision is much better than the one obtained with Fourier analysis.

2.3 Multifractal Spectrum

Several methods have been proposed to calculate \( f(\alpha) \) but in this case a direct determination of the \( f(\alpha) \), as suggested by Chhabra and Jensen [7], is preferable.

The following relationships were applied to calculate \( f(q) \) and \( \alpha(q) \) from the normalized measure:
\[ f(q) = \lim_{\delta \to 0} \frac{\sum_{i=1}^{n(\delta)} \mu_i(q, \delta) \log[\mu_i(q, \delta)]}{\log \delta} \quad (10) \]

\[ \alpha(q) = \lim_{\delta \to 0} \frac{\sum_{i=1}^{n(\delta)} \mu_i(q, \delta) \log[\mu_i(1, \delta)]}{\log \delta} \quad (11) \]

\( f(\alpha) \) is then obtained by plotting \( f(q) \) vs. \( \alpha(q) \) for each value of \( q \). Eq. 10 is essentially a restatement of the Boltzmann formula for statistical entropy when \( q = 1 \) at which value it is clear by comparison with Eq. 11 that \( \alpha(1) = f(1) \).

### 3 Results and Discussion

We present the ratio between the two main frequencies for LiNC/LiCN trajectories with initial conditions along the \( P_\psi = 0 \) cut on the minimum energy path, as a function of the angle variable \( \psi \). The frequency analysis has been carried out using three terms, over a time interval of 22 ps, and taking approximately 9000 points along the trajectories.

The determination of the multifractal spectrum \( (f(\alpha)) \) was done for each frequency ratio function calculated at each energy using always 10000 points. The studied energies were from the corresponding to the quantum states 20 to 100 with an increment interval of 20. Because the aim of this study was to compare the structure presented in the area selected in Fig. 1A, the analysis was done in the initial angle \( (\psi) \) range from 118 \((\psi_i)\) to 122 \((\psi_f)\) degree inclusive (Fig. 1B).

In Fig. 1A the results for one of the vibrational energy, 40, are represented. At this value of the energy we are in a mixed regime, where regions of regularity coexist with regions of well developed chaos. We find intervals in which the frequency ratio varies smoothly with the angular coordinate, and others in which it varies much more strongly. A section of this last one is shown in more detail in Fig. 1B.

Essentially what happens in the irregular region is that the classical motion of the system is chaotic, and the Fourier expansion is not able to parameterize this motion, since it does not take place on invariant tori.

At all energies studied, we took a common \( \psi \) interval inside the irregular region, and transform the frequency ratio, \( \nu_R/\nu_\psi \), in a probability measure, \( p_i \), into \((0,1] \) interval what is shown in Fig. 2 at two different energies. Latter we applied a multifractal analysis to study their irregular structure.

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![Graph](image.png)

Fig. 1 Frequency ratio as a function of the initial angle \( \psi \) for an ensemble of trajectories started along \( P_\psi = 0 \) cut on the minimum energy path of the LiNC/LiCN isomerization system at the energy of 3122.3 cm\(^{-1}\) corresponding to the 40\(^{th}\) quantum state.

![Graph](image.png)

Fig. 2 Probability measure, \( p_i \), into \((0,1] \) got from the frequency ratio of the irregular region selected in Fig. 1B. Part A correspond to the energy of the quantum state 20 and part B to the 40.
In Fig. 3, the measure (FM) shows a multifractal character at all the energies. The convex function $f(\alpha)$ varies between energies pointing out the different richness of the studied structure. In earlier works [8] the scaling structure of power spectra of dynamical systems has been studied using a similar analysis and showing a multifractal nature too.

![Fig. 3 Multifractal spectra of the measure (FM) at the energies 2299.0 cm$^{-1}$, 3122.3 cm$^{-1}$, 3702.7 cm$^{-1}$, 4167.2 cm$^{-1}$, 4596.0 cm$^{-1}$ corresponding to the quantum states 20(full square), 40(full circle), 60(full diamond), 80(full triangle), 100(empty square).]

One way to see the variations in complexity between energies is to plot the amplitude ($\alpha_{\text{max}}-\alpha_{\text{min}}$) reached by the spectrum in each one (Fig. 4).

![Fig. 4 Multifractal amplitude ($\alpha_{\text{max}}-\alpha_{\text{min}}$) as function of the energy given as the quantum energy level.]

The overall trend is to increase the complexity, though this one is not smooth. From 20 to 40, the amplitude increases and at 60, the amplitude value is close to the value for 20. Then from 60 to 100 the trend looks constant.

4 Conclusions

The frequency map shows a clear multifractal character at different vibrational energies. However, the complexity presented in the spectrum at each energy varies in a non constant fashion. It is logical to think that the multifractal character will increase when the tori are being destroyed, since the presence of cantori increase and they are the responsible of this fractal feature.

In the situation that the cantori haven’t an strong influence and the trajectory is ergodic in shorter time intervals, this fractal character begins to diffuse. The multifractal analysis of FM has pointed out this phenomena.

The analysis of the FM evidences the presence of cantori, with more or less influence at different energies, which produce a non constant $\alpha_{\text{max}}-\alpha_{\text{min}}$ variation among the energies studied. This variation should tend to the value corresponding to a random distribution of frequencies when the energy tends to infinite. Further research is necessary to determine a more detailed study of these behavior at different energies.

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