Unveiling the chaotic structure in molecular systems using Lagrangian descriptors

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The phase space structure of a dynamical system determines, among other issues, its regular or chaotic behavior, and then several indicators have been developed in order to correctly detect, characterize, and analyze it. Among them, the illustrative Poincaré surface of section (PSOS) or the more quantitative Lyapunov exponents [1] are worth mentioning.

In this communication, published in [2], we apply the Lagrangian descriptor method [3, 4], defined by the p-norm of a dynamical flow $\dot{\mathbf{z}} = \mathbf{f}(\mathbf{z}, t)$ as

$$M_p(\mathbf{z}_0, t_0, \tau) = \int_{-\tau}^{\tau} dt \sum_{i=1}^{n} |\dot{z}_i|^p, \qquad (1)$$

where $p \leq 1$, and τ is the integration lapse of time to unveil the chaotic structure of the phase space of the LiNC⇌LiCN isomerizing molecular system, using the two degrees-of-freedom (2-dof) Hamiltonian model [5] defined by

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

where R is the distance between the Li and the center of mass of the C-N fragment, r the C-N distance (hold frozen at its equilibrium value r_{eq} in the 2-dof approximation), θ the angle between them. P_R, P_θ (and P_r in the 3-dof version) are the corresponding conjugate momenta and $\mu_{1,2}$ the Li-CN and C-N reduced masses, respectively. The potential energy surface $V(R, r_{\text{eq}}, \theta)$ exhibits two wells, one at $\theta = \pi$ rad corresponding to the most stable isomer with linear configuration Li-NC, and the other at $\theta = 0$ rad for Li-CN. Along the minimum energy path $R_{\text{MEP}}(\theta)$ joining these two wells there is a saddle with triangular configuration that appears at $\theta \simeq 0.28\pi$ rad. We also study the importance of different effects in the definition (1), such as using p-norms instead of the *standard* one, or the magnitude of the integration time lapse.

Some results for the (ψ, P_ψ)-PSOS computed for $\rho = 0$ and $\dot{\rho} > 0$ and $E = 4000$ cm^{-1}, using the following canonical transformation

$$\begin{aligned} \rho &= R - R_{\text{MEP}}(\theta), \quad & P_\rho &= P_R, \\ \psi &= \theta, & P_\psi &= P_\theta + \left(\tfrac{dR_{\text{MEP}}}{d\theta}\right)_{\theta=\psi} P_\rho, \end{aligned} \qquad (3)$$

are shown in the panel (a) of the figure. In it, the existence of two regions of regular motion at the isomers, embedded in a sea of chaos, is apparent. In panel (b) we show the corresponding values of the Lagrangian descriptor for trajectories starting at points in the PSOS. Notice the ability of Lagrangian descriptors to identify the different structures in phase space, such as in the areas of regularity at the isomers and at $\theta \simeq 0.6\pi$ rad, or even more striking of the homoclinic tangle originated at the saddle; this fact is explained since the Lagrangian descriptors present singularities along the invariant manifolds, which render abrupt changes in the colormap in (b).

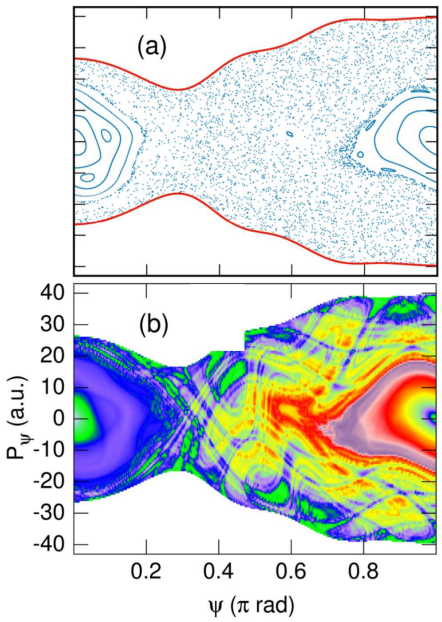

Fig. 1. Composite Poincaré surface of section (a), and Lagrangian descriptors (b) for the 2-dof model ($r = r_{\text{eq}}$, $P_r = 0$ a.u.) of the LiCN/LiNC molecular system. The computations have been performed by setting in Eq. (1) $p = 0.4$ and $\tau = 2 \cdot 10^4$ a.u. for a vibrational energy equal to E = 4000 cm^{-1}.

Finally, we have also applied the Lagrangian descriptors to study a more accurate model of our molecular system that includes the three vibrational dof's, i.e., not freezing r at its equilibrium value in (2, where the popular and useful PSOS method cannot be applied. Results will be presented at the conference.

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