# Influence of the laser frequency in the nonlinear dynamics of the HCN molecule

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One topic of much interest is the active control of molecular nonlinear dynamical systems and chemical reactivity, typically using lasers.

In relation with the HCN molecule, the laser control of bond excitation, bond dissociation (typically of the strong CN bond), and the isomerization of HCN has been extensively considered in the literature. The works in references [1] and [2] are most relevant for the present study. We extend the analysis by considering the influence of the laser frequency in the dynamics, in order to check the possibility of using it as a possible control parameter by varying the dynamical structure of the system. In this way, we can be more precise than previous works in predicting which laser frequencies are best in order to promote dissociation [2]. Let us remark, that this is not an easy task from the theoretical point of view, since the dynamical problem consists of more than two degrees of freedom.

We use a minimal 2D linear model for the H-C-N molecule, consisting only of the two stretching modes. The resulting dynamics are described by a classical Hamiltonian. An additional term, $H_I$, associated to the actuation of a monochromatic laser, is introduced, and thus, the description of the whole system is given by

$$H(t) = H_0 + H_I = T + V + H_I(t), \qquad (1)$$

where $T$ is the kinetic energy term, the potential energy, $V$, consists of two uncoupled Morse functions. and the interaction with the laser, $H_I(t)$, is described within the dipole approximation as

$$H_I = \lambda_F \ \mu(q_1) \ \cos\omega_F t \qquad (2)$$

being $\omega_F$ the frequency of the laser field, $\lambda_F$ its amplitude, and $\mu(q_1)$ the HCN dipole function. In this way the dimensionality of our system is $N = 2.5$.

We have analyzed the behavior of this dynamic system using the Small Alignment Index (SALI). In Fig. 1 and 2 we present the results of this analysis for the vibrational energy $E = 0.135$ a.u. In each plot a uniform grid of 10,000 initial conditions within the available Poincare surface of section corresponding to the system without laser was used as starting points to propagate the corresponding trajectories.

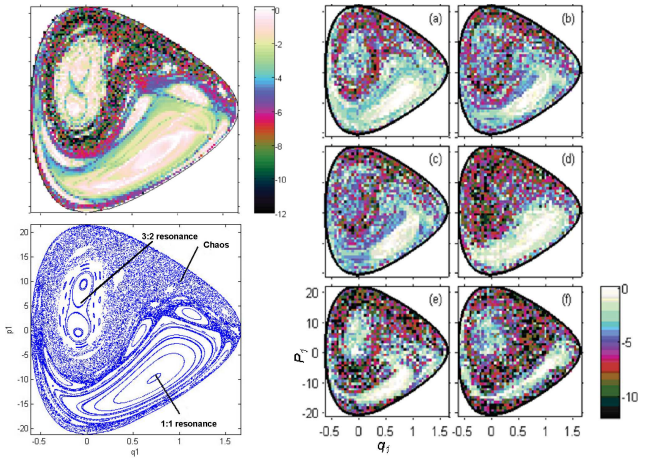


Figure 1: Left panel (without laser): Composite Poincaré surfaces of section corresponding to intersections of trajectories with the plane $q_2 = 0$ with $P_2 > 0$ (botton) and SALI colored map (top); Right panel: SALI colored maps for HCN in the presence of a laser with the following values of the frequency: $\omega_F = 0.003333$ (a), 0.004123 (b), 0.009278 (c), 0.010000 (d), 0.014430 (e), and 0.018556 (f). Values are shown using the color code given on a logarithmic scale at the right of the plots.

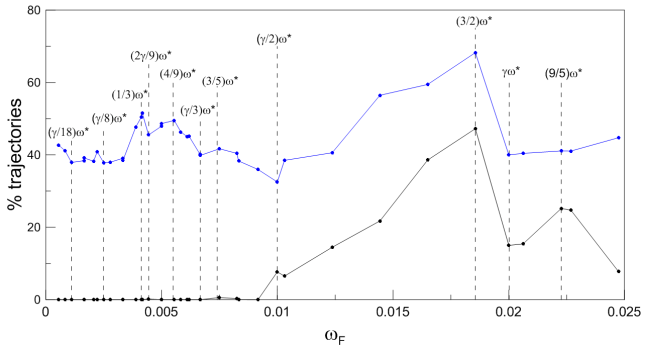


Figure 2: Fraction of dissociative (black circles) and chaotic (blue circles) trajectories as a function of the laser frequency, $\omega_F$. All peaks and valleys are found to be correlated with resonances between $\omega_F$ and $\omega^*$. Being $\omega^*$ the corresponding frequency to the 1:1 resonance in the system without the laser.

[1] R. Brezina and W.-K. Liu, J. Phys. Chem. A **108**, 8852 (2004).

[2] A. Sethi and S. Keshavamurthy, Mol. Phys. **110**, 717 (2012).

[3] A. Lopez-Pina, J.C. Losada, R.M. Benito and F. Borondo, J. Chem. Phys. **145**, (24) 244309 1-12 (2016)