Laser Driven Nonlinear Dynamics and Bond Breaking of the HCN Molecule

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We study the vibrational dynamics of a model for the HCN molecule in the presence of a monochromatic laser field. The variation of the structural behavior of the system as a function of the laser frequency is analyzed in detail using the smaller alignment index, frequency maps, and diffusion coefficients. It is observed that the ergodicity of the system depends on the frequency of the excitation field, especially in its transitions from and into chaos. This provides a roadmap for the possibility of bond excitation and dissociation in this molecule [1].

Molecular vibrational dynamics has been the subject of an intense research activity in the past years, this giving rise to numerous publications that appeared in this field. The theoretical framework for these kinds of studies is based both on classical and quantum mechanics, having profound roots in the characterization of chaos in Hamiltonian systems. This topic was nicely addressed in the seminal work of Kolmogorov, Arnold, and Moser, that produced the celebrated KAM theorem. The study of dynamical chaos theory has substantially flourished thereupon, becoming an area of active research within the scientific community of dynamical systems.

One topic of much interest in this branch of chemical dynamics is the active control of molecular nonlinear dynamical systems and chemical reactivity, typically using lasers. An extensive literature has been produced on this subject. In relation to our work with the HCN molecule, the laser control of bond excitation, bond dissociation (typically of the strong CN bond), and the isomerization of HCN have been extensively considered in the literature [2]. In the first paper, Brezina and Liu considered the possibility of controlling the CH and CN excitations and dissociation with laser pulses. For this purpose, they used a classical mechanics widespread vibrational model consisting of two kinetically coupled Morse bond functions freezing the bending at its equilibrium value. Special attention was paid to the role played by IVR, considering different values of the laser frequency and amplitude. These authors found that simple linearly chirped pulses are effective in exciting and dissociating the CH, while this is more difficult for the stronger CN bond. Recently, Sethi and Keshavamurthy revisited the same problem, concentrating only in one of the laser frequencies. This work was a start in the identification of the main aspects of the dissociation dynamics and mechanism in phase space, and the characterization of the system in terms of the classical dynamical resonances (Arnold) network. They found the importance of two regions of frequency space, the dissociation hub, which constitutes a gateway for dissociating trajectories, and the noble hub, characterized by very irrational frequency ratios, that constitutes a very sticky area of trapped trajectories for long times.

In this paper, we extend previous work, by considering the influence of the laser frequency on the dynamics, to use 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.

References


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