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Femtochemistry - some reflections and perspectives

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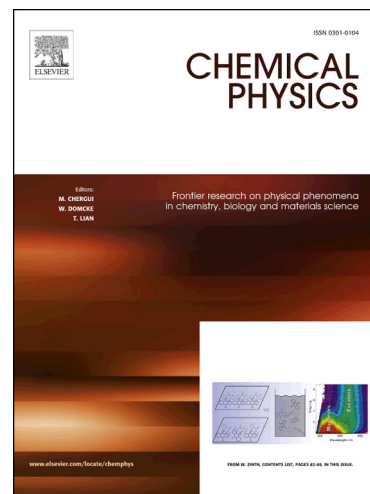
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In this perspective we highlight some aspects of femtochemistry, that is, the creation, detection and control of non-stationary states in chemical dynamics. Some recent results are discussed with a view on the challenges and pending scientific questions. We discuss theoretical as well as experimental issues with the emphasis on laser control of chemical dynamics, in the weak-field and strong-field regimes.

I. INTRODUCTION

For many years, the experimental observations of spectroscopy and photochemistry were interpreted in terms of the stationary molecular eigenstates of the molecular Hamiltonian. However, due to the seminal work of E.J. Heller [1], it became clear that the spectroscopy and photochemistry of electronic transitions, e.g., absorption or Raman spectroscopy and final product distributions for a photofragmentation process, can all be interpreted as signatures of the dynamics of the so-called Franck-Condon wave packet. A wave packet is a non-stationary state - which can be represented as a coherent superposition of the stationary molecular eigenstates. In an electronic transition from an initial nuclear state associated with the electronic ground state to an excited electronic state, the Franck-Condon wave packet can be represented by

$$|\psi_{\text{ex}}(t)\rangle = \exp(-i\hat{H}_{\text{ex}}t/\hbar)|\Phi(0)\rangle \quad (1)$$

where $|\Phi(0)\rangle$ is the product between the initial nuclear state and the projection of the electronic transition dipole moment along the direction of a plane polarized electric field, and \hat{H}_{ex} is the Hamiltonian associated with nuclear motion in the excited electronic state(s), see Fig. 1.

It was also shown that during the interaction with cw (continuous wave) lasers excited stationary molecular eigenstates are created, whereas the creation of a wave packet like the one in Eq. (1) would require an interaction with an ultrashort femtosecond pulse. Nevertheless, this indirect approach to light-induced chemical dynamics [1, 2], showed us that we can see the signatures of dynamics even without actually creating the Franck-Condon wave packet.

The groundbreaking work of A.H. Zewail [3] and co-workers led to the creation of femtochemistry. Here the goal is to create, detect and control the time evolution of non-stationary states of matter. The creation and control of wave packets are accomplished via interaction with pulsed electromagnetic fields. With a few exceptions, like detection of non-stationary states via time-resolved electron diffraction, the detection is also based on the interaction with pulsed electromagnetic fields.

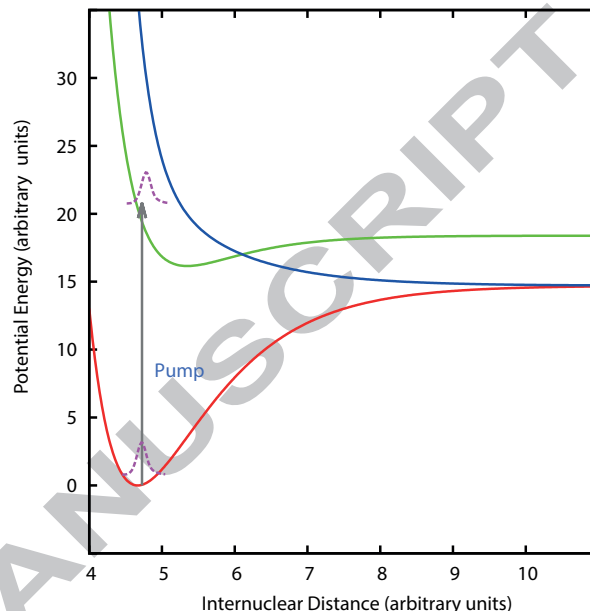


FIG. 1: The vertically excited initial state, the so-called Franck-Condon wave packet of Eq. (1) at $t = 0$.

The non-stationary states of particular relevance to femtochemistry include, of course, as a central theme the dynamics of the chemical bond, i.e., bond making and bond breaking. However, all types of non-stationary states including rotational, vibrational, and electronic of isolated molecules, as well as non-stationary states of solvents and solids are of interest - as long as they contribute to our understanding of chemistry and biology. Creation and control of wave packets are closely related since the same pump laser is used for both aims, in the latter case using relevant control knobs of the laser. If control is not the goal, the pump pulse is typically a transform-limited Gaussian pulse and in the ultrashort pulse limit, the Franck-Condon wave packet is created.

Femtochemistry is often subdivided into structural dynamics and reaction dynamics. Structural dynamics is focusing on the direct determination of the time-dependent atomic positions. The scope of reaction dynamics is broader, it includes, e.g., the study of energy flow between various electronic states. Femtochemistry, like photochemistry, typically starts with an electronic transition and a reorganization of the valence electrons within

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