Ultrafast Photoinduced Dynamics mediated by Conical Intersections

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It is well known that the most general case of photo-induced chemical reactions occurs through non-adiabatic molecular dynamics. The complex panorama of potential energy surfaces describing the excited states of polyatomic molecules is characterize quite often by non-adiabatic crossings and the presence of multiple conical intersections. A conical intersection (CI) is a 3N-8 dimensional hypersurface of intersection between two electronic states. The two remaining internal coordinates, *i.e.*, **g** as the difference gradient vector, and **h** as the non-adiabatic coupling vector, define the branching plane.

Conical intersections can be considered as the transition states of electronic excited states and therefore the coupling between the different degrees of freedom, valence electrons and vibrations, and the timescales of these motions, are of the highest interest to understand photochemistry. The aim is to find an equivalent of the “Polanyi rules” for excited state polyatomic dynamics, in such a way that specific vibrational dynamics at conical intersections would be as important to dynamics as are the topographical features of the conical intersections themselves.

In the present case, we highlight several cases of non-adiabatic reaction dynamics in which CIs are determining steps for the photoinduced dynamics. Time scales for bifurcation through the conical intersection in the wave packet dynamics of methyl iodide using time-resolved Coulomb explosion imaging [1] and attosecond transient absorption spectroscopy [2], light induced conical intersection in methyl iodide [3] and non-adiabatic dynamics in vinyl iodide [4].

Index Terms: Photochemistry, non-adiabatic dynamics, Coulomb explosion, transient absorption, light induced conical intersection.

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