

MAPPING EXTENDED REACTION COORDINATES IN PHOTOCHEMICAL DYNAMICS

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Modern laser sources facilitate a wide range of experimental strategies for interrogating the complex non-adiabatic dynamics operating in the excited states of molecules. Developing detailed insight into such processes is vital in understanding various fundamental processes of biological, environmental, and technological significance. Measurements may be broadly separated into frequency- and time-resolved variants, with a combination of different approaches (with different associated observables) typically being required to reveal a complete mechanistic picture. In the former category, quantum state-resolved information may often be obtained using narrow linewidth lasers. This provides detailed information relating to the starting point on the photochemical reaction coordinate (via the absorption spectrum) and the asymptotic endpoints (i.e. the photoproducts). No direct observation of the intermediate pathways connecting these two limits is generally possible, though, due to the inherently long temporal duration of the laser pulses relative to the typical timescales of non-adiabatic energy redistribution processes. It is therefore desirable to obtain complementary information that monitors real-time evolution along the reaction coordinate as excited state population traverses the potential energy landscape. This may be achieved in time-resolved pump-probe experiments conducted using laser pulses with temporal durations comparable to the ultrafast (i.e. sub-picosecond) timescales of vibrational motion. The use of valence state photoionization for the probe step is a commonly employed methodology and has proved highly instructive in revealing subtle mechanistic details of key energy redistribution pathways operating in a wide range of molecular systems. One common limitation in such measurements, however, is the restricted “view” along the reaction coordinate(s) connecting the initially prepared excited states to various photoproducts. Guided by examples drawn from our own recent work using time-resolved photoelectron imaging, this talk will discuss such issues in detail and highlight some new directions that potentially help overcome them – with particular emphasis placed on the advantages of projecting as deeply as possible into the ionization continuum. The role of complementary measurements using other spectroscopic techniques and the importance of high-level supporting theory to guide data interpretation will also be reinforced.