

Ultrafast Ion Chemistry

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In this talk we will discuss the applications of femtosecond time-resolved photofragmentation spectroscopy^{[1], [2]} to ultrafast photoionization-induced uni- and bi-molecular ion chemistry. In this method, a femtosecond pump pulse first produces an ensemble of positive ions via photoionization of the neutrals. Owing to the structural difference between the ionic and neutral ground states, vertical femtosecond photoionization can prepare an initial wave packet far away from the global equilibrium structure of the cation. The initial wave packet then evolves on the ionic surface and may undergo rearrangement (reaction) and dissociation, depending on the deposited energy and the nature of the ionic surface. A delayed probe pulse then brings the evolving cationic system to higher ionic states that ultimately undergo fragmentation. The ionic dynamics can be detected by monitoring either the parent-ion depletion or fragment-ion formation as a function of the pump-probe delay time, provided that the probing transition varies along the reaction coordinate. This fs-pump-probe photoionization-photofragmentation scheme is simply the time-domain version of ion photofragmentation spectroscopy and is most suitable for studying photoionization induced ultrafast ion chemistry. It is based on the general fact that the molecular nuclear and electronic structures often exhibit significant changes upon removal of an electron. In well-designed molecular systems, these changes may correspond to important elementary steps, including isomerization, proton transfer, and charge transfer.

Applications of this technique to photoionization-induced azobenzene cation twisting isomerization^[1] and proton transfer (PT) between phenol cation and ammonia^[2] will be discussed. In the case of the PT system,^[2] neutral PhOH-NH₃ complexes prepared in a free jet were photoionized by femtosecond 1+1 REMPI using phenol as the chromophore, and the subsequent dynamics occurring in the cations was probed by

delayed pulses that result in ion fragmentation. The experiments revealed that PT in [PhOH-NH₃]⁺ cation proceeds in two distinct steps: an initial impulsive wave-packet motion in ~70 fs followed by a slower relaxation of about 1 ps that stabilizes the system into the final PT configuration. These results indicate that for a barrierless PT system, even though the initial PT motions are impulsive and ultrafast, the reaction may take a much longer time scale to complete.

References

- [1] J.W. Ho, W.K. Chen, and P.Y. Cheng, *J. Chem. Phys.*, 131, 134308 (2009).
- [2] C.C. Shen, T.T. Tsai, J.W. Ho, Y.W. Chen, and P.Y. Cheng, *J. Chem. Phys.*, 141, 171103 (2014).

