

GEOMETRY-DEPENDENT MOLECULAR PHOTOIONIZATION DYNAMICS

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A significant part of Chemistry is aimed at understanding the geometry and reactivity of molecules. To this end, understanding how the electronic structure of molecules changes as the molecules are distorted, or as chemical bonds are broken or formed, is of fundamental importance. The classic works of Mulliken^{1,2} and Walsh³ showed how even a qualitative understanding of the geometry-dependence of molecular orbitals allowed the prediction of molecular geometries, and these ideas were ultimately developed into molecular theories of chemical reactivity by Fukui, Woodward and Hoffman, and others.⁴ The geometry dependence of molecular structure also has numerous manifestations in valence- and inner-shell photoionization dynamics, perhaps most notably in efforts to correlate shape resonances with bond lengths, but also in a large number of symmetry-breaking or vibronically induced effects.⁵ While many experiments have confirmed the utility of their approach, until recently, direct experimental methods to probe the geometry dependence of orbital energies have been scarce. With the development of ultrafast time-domain techniques, it has been possible to use pump-probe techniques with vibrational wavepackets to determine how electronic structure and reactivity depends on reactivity.⁶ Ultrafast fourth-generation sources such as the LCLS will allow pump-probe wavepacket techniques to be extended into the hard x-ray regime. The advantage of such studies is that the initial state is a localized orbital, allowing more direct analysis of delocalized final states. I will discuss some potential experiments using such sources.

Although the pulse durations of current third-generation light sources are not sufficiently short to make practical wave-packets, pump-probe studies can still provide insight into the geometry-dependence of the electronic structure, and into symmetry-breaking and vibronically induced effects in inner-shell photoionization. I will discuss pump-probe experiments that make use of the infrared-pump/x-ray probe technique that was recently demonstrated by Qian et al. at the Advanced Light Source. Although not strictly time-domain experiments,

such work will provide the foundation for experiments when fourth generation light sources come on line.

References

1. Mulliken RS. 1928. *Phys. Rev.* 32:186-222.
2. Mulliken RS. 1932. *Rev. Mod. Phys.* 4:1-86.
3. Walsh AD. 1953 *J. Chem. Soc.* 2260-2330.
4. T. A. Albright, J. K. Burdett, and M. Y. Whangbo, *Orbital Interactions in Chemistry* (Wiley, New York, 1985).
5. J. A. Stohr, *NEXAFS Spectroscopy* (Springer, New York, 1996).
6. A. H. Zewail, *J. Phys. Chem.* **100**, 12701 (1996).
7. X. M. Qian, A. H. Kung, T. Zhang, K. C. Lau, and C. Y. Ng, *Phys. Rev. Lett.* **91**, 233001 (2003).

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