X-RAY PROBES OF ELECTRONIC STRUCTURE IN REACTING SYSTEMS

Stephen T. Pratt
Argonne National Laboratory, Argonne, IL 60439

One of the goals of modern Chemistry is to understand how electronic structure generates the forces that maintain the geometry of stable molecules, or drives particular reaction to new chemical products, i.e., to understand how chemical bonds are created, preserved, rearranged, and broken. Even during the course of a simple bond dissociation process, electronic structure can evolve in very complex manners. Thus, while many electronic structure methods can reproduce the equilibrium geometry of most molecules, the accurate description of the evolution of electronic structure from the molecule to dissociation fragments can require some of the most advanced methods available. As a result, experimental probes that can probe how electronic structure changes with geometry are extremely valuable, especially when they are applicable far from equilibrium geometries. This is one reason for the excitement over pump-probe techniques that have combined visible/ultraviolet excitation and x-ray probes, in which x-ray absorption spectroscopy and scattering can provide information on how the electronic structure and geometry of the molecule changes as a function of time after excitation takes place. Pushing the time domain of such studies into the few femtosecond regime will ultimately be required to probe vibrational wavepackets in molecules built from first-row elements, and to test key aspects of the evolution of electronic structure through the course of a reaction. There is also a growing desire to push the time resolution into the attosecond regime to probe the evolution of electronic wavepackets. The development of hard x-ray free electron lasers such as the LCLS, along with the development of laboratory-scale x-ray sources based on high-harmonic generation, are beginning to make such experiments a reality.

Tunable, short-pulse, high-intensity x-ray sources that can be synchronized with visible, ultraviolet, and ultimately other x-ray sources, will provide (an to some extent are already providing) unprecedented tools to study how electronic structure changes as a function of the geometry of a molecule. As one example, shape resonances in x-ray absorption experiments are known to provide information on molecular bonding, and can be sensitive to both molecular geometry and electronic structure. The new pump-probe techniques could be used to characterize their behavior for a wide range of controlled geometries, as well as for a wide range of electronic structures. As an illustration, consider the absorption spectrum of carbon monoxide near the carbon K edge. There is an intense pre-edge feature corresponding to excitation to a π^* shape resonance, as well as an intense broad feature above the edge corresponding to excitation to a σ^* resonance. As seen in Figure 1, similar features are observed in other molecules with a

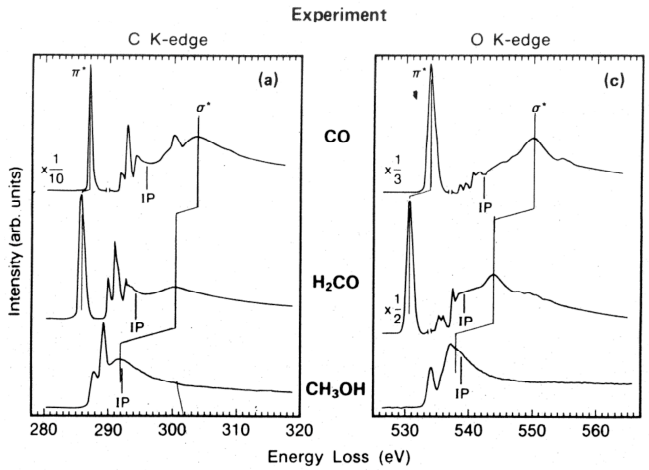

Figure 1. From J. Stöhr, *NEXAFS Spectroscopy*, Springer, New York (1992),

CO bond. Synchronized visible/uv and x-ray ultrafast sources would first allow the use of stimulated emission pumping to create vibrational wavepackets on the ground electronic state surface of CO by using the first laser, and the recording of the near-edge spectrum as a function of time delay with the x-ray source. This approach would allow one to see how the resonances change as a function of the CO bond length in the ground electronic state. In addition, vuv techniques could be used to populate valence excited states of the CO, and analogous time-resolved studies could be used to determine how the shape resonance is influenced by geometry in these excited configurations. Valence shell photoionization of the CO at select wavelengths could also be used to prepare CO^+ in select electronic states, and x-ray absorption spectra would thus probe the resonance structure in these configurations. With extreme ultraviolet sources, it would also be possible to perform analogous experiments on CO^+ with inner valence holes. Some of these states dissociate quite rapidly, but it may be possible to capture the structure along the dissociation path. Finally, the high intensity of the LCLS source has generated considerable interest in double core-hole states. For sufficiently high intensities, it is possible to create two core holes sufficiently quickly that the second is formed before the first is filled by Auger decay or fluorescence. The ability to record near-edge absorption spectra for CO with a 1s hole on either the C or O would again provide considerable insight into the electronic structure of this system. Ultimately, such understanding may lead to the ability to control the production of double core holes in more complex systems, along with the ability to control the fragmentation patterns resulting from their decay.