

Ultrafast Excited-State Processes in Inorganic Systems

Guest Editorial for the *Accounts of Chemical Research* special issue on “Ultrafast Excited-State Processes in Inorganic Systems”.

Since Alfred Werner first defined the concept of a coordination compound in 1893, transition metal complexes have captured the interest and imagination of generations of chemists. Once the sole purview of Inorganic Chemistry, the study of transition-metal-containing systems now spans research in materials science, catalysis, biology, and energy science just to name a few. Their relevance in such a range of areas stems largely from the widely variable electronic structures that characterize metal complexes; this in turn is a reflection of the diverse array of components that comprise this class of molecules. From ligand-localized features reminiscent of organic compounds to charge-transfer and redox behavior that facilitate their use in solar energy conversion strategies, complexes of the d-block simultaneously present chemists with great challenges and great opportunities.

Perhaps nowhere is this dichotomy more evident than in the application of ultrafast spectroscopy to the study of the photophysics of transition metal compounds. The earliest applications of picosecond (and later femtosecond) spectroscopic methods largely focused on metal carbonyls, in part due to their synthetic accessibility at a time when the technology represented the most demanding aspect of the science. Coordination chemistry began to merge with modern ultrafast science in the late 1990s, when femtosecond time-resolved absorption spectroscopy was used to characterize for the first time the ultrafast nature of excited-state evolution in the ubiquitous inorganic chromophore $[\text{Ru}(\text{bpy})_3]^{2+}$.¹ As advances in instrumentation made the technology more readily accessible, the rich nature of inorganic photophysics that exists on ultrafast time scales began to become evident as research efforts shifted toward the study of systems that had a more direct connection to photoinduced processes of broader interest to the chemical community. Suddenly it became possible to investigate light-induced reactions in the ultrafast time domain where the fastest fundamental chemical processes such as changes of electronic states and molecular vibrations occur. This window into the earliest stages of excited-state dynamics has led to a new understanding of how inorganic chromophores respond to the absorption of light, while at the same time challenging decades-old assumptions concerning the relative rates of processes such as internal conversion, intersystem crossing, and even the very nature of the interplay between electronic and nuclear degrees of freedom that constitute the basis of fundamental concepts such as the Franck–Condon principle and Born–Oppenheimer approximation. From the perspective of inorganic chemistry (the lens through which this Special Issue is being viewed), ultrafast time-resolved spectroscopy has thus evolved from being a research project in and of itself to an important tool for examining the excited-state chemistry of transition metal-containing compounds.

Today, ultrafast spectroscopic methods comprise a remarkable range of techniques, many of which have found their most exciting realizations through their application to inorganic chromophores. An excellent example is the development of picosecond and femtosecond time-resolved X-ray methods. Inorganic compounds can exhibit some of the largest photoinduced structural changes known; these structural changes are ideally suited for examination with structure-specific probes such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption (XAS) spectroscopies. And what chemist is not fascinated by the notion of being able to visualize the structural evolution of their compound in real time? More recent has been the development of femtosecond X-ray fluorescence, a technique that has been shown to provide information concerning the spin of the excited state being sampled: given the dominant role of intersystem crossing in the excited-state dynamics of inorganic systems, this method, which in many ways complements and amplifies the well-established technique of fluorescence upconversion, promises to play an increasingly important role as the field continues to develop. Vibrational techniques—both infrared absorption and Raman—have also become more prominent over the past decade. With regard to the latter, work pioneered by Richard Mathies has extended Raman spectroscopy into a regime previously thought to be unattainable through femtosecond stimulated Raman scattering (FSRS), offering new possibilities for the study of excited-state dynamics that combine the temporal resolution of ultrafast with the state-specificity of resonance Raman. Two-dimensional electronic and vibrational techniques are a more recent addition to the mix with their ability to yield insights into the coupling of various degrees of freedom over the course of excited-state evolution. All of this new information is providing a wealth of opportunities for the theoretical community, where the advent of time-dependent wavepacket dynamics simulations, time-dependent DFT, and nonadiabatic dynamics are helping experimentalists gain a more sophisticated understanding of the excited-state properties of their systems while at the same time advancing theoretical methodologies and posing important new questions concerning the degree to which one might ultimately control excited-state evolution in complex inorganic chromophores. Many of the individuals who have pioneered efforts in these various areas are represented in this volume.

This Special Issue evolved from a symposium we organized through the ACS Division of Inorganic Chemistry at the National Meeting of the American Chemical Society in New Orleans in April of 2013. The idea was to bring together as many of the major practitioners of ultrafast methods—both experiment and theory—studying the photophysics and

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photochemistry of inorganic compounds. The result is a representative overview of current research on various aspects of this exciting and rapidly developing area of chemistry. The contributions span fundamental studies of (relatively) simple molecules to more complex systems geared toward applications in solar energy conversion. Intersystem crossing is a recurring theme of contemporary ultrafast studies as evidenced by the number of groups working on various manifestations of this important excited-state process. The remarkably fast photo-induced low-spin to high-spin conversion of Fe(II) chromophores is surveyed by Chergui, stressing the application of emerging X-ray techniques. Photoinduced spin changes in iron complexes are also discussed by Gaffney et al., who compares them to electron localization dynamics in charge transfer states, and in the process highlighting the use of time-resolved X-ray fluorescence and polarized IR absorption. Solid-state systems are studied by Collet et al., in which combined ultrafast X-ray and optical absorption studies of a crystalline iron(II) material suggest a role for electron–phonon coupling in spin-crossover dynamics. Singlet-to-triplet conversion (as opposed to the singlet–quintet conversion that characterizes the dynamics in the iron-based chromophores) is discussed in several articles. Detailed theoretical treatments are provided by Tavernelli and Daniel et al., who use nonadiabatic molecular dynamics and wavepacket approaches, respectively, to uncover details not readily discernible from experiment. Theoretical and experimental studies alike tend to agree on the importance of electron–vibrational coupling and medium fluctuations in promoting intersystem crossing. Several contributions deal with spectroscopic characterization of singlet and triplet excited states of disparate orbital parentages and localizations, together with their relaxation and deactivation processes where spin-change is again an important step. These processes are manifested in systems ranging from charge-transfer complexes of ruthenium(II), rhenium(I), and osmium(II) (Chergui), platinum(II) (Cannizzo et al.), copper(I) (Tahara et al.), as well as the unusual case of metal–metal to ligand charge transfer and $\delta\delta^*$ states of quadruply bonded molybdenum and tungsten(II) complexes (Chisholm et al.). The importance of solvent (i.e., medium) dynamics in excited-state evolution is stressed by a two-dimensional infrared study of electronic excited states of rhenium(I) chromophores (Kubarych et al.). Net chemical changes involving bond breaking and forming is another possible outcome of charge transfer excitation, whose course often is determined by the primary ultrafast steps. Photo-induced isomerization of sulfoxide ligands in ruthenium(II) complexes is a representative case, as discussed by Rack et al.

The journey through excited states and their dynamics continues by discussing the interplay of excitations localized at a metal complex and covalently appended organic dye molecule (Castellano), and between metal- and ligand-localized states of iron(III) porphyrins and cobalamins, the latter undergoing ultrafast splitting of a cobalt–alkyl bond (Sension et al.). Photoinduced electron transfer is another important topic. Vlček et al. presents several cases where photoinduced electron transfer in molecular assemblies containing a rhenium-based chromophore is accelerated by coupled vibrational motions or by enhanced electronic coupling. Weinstein et al. focus on intramolecular flows of vibrational energy initiated by charge transfer excitation and presents a remarkable finding of electron-transfer control by specific vibrational excitation of a bridging group between the donor and acceptor. The latter two

articles also highlight the potential of one- and two-dimensional time-resolved infrared spectroscopy in electron-transfer studies.

Efficient charge separation is, of course, a prerequisite for photochemical solar energy conversion. One of the most important issues is the multielectron nature of important reactions such as water splitting and carbon dioxide reduction. This problem is addressed by Hammarström who examines accumulation of electrons in complex assemblies containing multiple chromophoric, redox and catalytic sites, either purely molecular or associated with n- and p-type semiconductors. Processes related to solar conversion also are the topics of articles by Papanikolas et al., who discusses electron and energy transfer in polymeric structures containing multiple ruthenium chromophores in contact with titanium dioxide, while the contribution by Lian et al. investigates exciton and electron dynamics in semiconductor nanorods where the photo-generated charges are ultimately used to generate hydrogen and oxygen. Last but not least, this Special Issue also shows that theory is currently reaching the level where it can explain and predict structures and dynamics of electronic excited states. Besides the two aforementioned articles by Tavernelli and Daniel, quantum chemical calculations are reported in several other articles, providing insights into electron and spin distributions in excited states as well as on dynamic medium effects.

We hope that this Special Issue serves to illustrate the remarkable research that is currently underway at the interface of ultrafast science and inorganic chemistry. It is a vibrant area for discovery that is continuing to attract researchers from disciplines ranging from physics to chemistry to biology. Much like the light sources that are being used to study these chemical systems, the future of this field is bright indeed.

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Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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