Inorganic Chemistry

Forum Article

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Preface for the Forum on Insights into Spectroscopy and Reactivity from Electronic Structure Theory

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In recent years, there have been major advances in quantum chemistry methods, including their implementation in numerous user-friendly codes and improvements in computer power and the general availability of supercomputers. On the basis of these advances, quantum chemistry is having an ever-increasing impact in the field of inorganic chemistry, a fact that has catalyzed the concept of this Forum issue. We have recruited 10 of the leading computational chemists who focus on exciting areas of contemporary inorganic chemistry to contribute. Their presentations are broadly divided into two categories. The first emphasizes the methodology relevant to spectroscopy and reactivity, while the second is directed more toward using computational methods to understand reaction mechanisms. All contributions reflect the state of the art in theoretical inorganic chemistry.

The focus of the first part of this Forum issue is on the computational methods but also includes highly relevant and timely applications. The contribution by Van Voorhis and colleagues[1] emphasizes computational thermochemistry using density functional theory (DFT) with application to the water-splitting reaction. This thoughtful presentation deals with the accurate calculation of reduction potentials and the importance of the explicit inclusion of solvent, particularly when hydrogen bonding makes a significant contribution. It is demonstrated that DFT thermodynamics can provide insight into trends in reactivity, for example, in the volcano plots for the first transition series in Figure 5 of the article, which illustrates a Sabatier analysis[2] of overpotentials for water oxidation in terms of increasing substrate and decreasing product interactions with the catalyst. Computational results for specific oxygen-evolving reactions for the Nocera et al.[3−5] cobalt oxide and the Meyer et al.[6−8] binuclear and mononuclear ruthenium catalysts are discussed in terms of nucleophilic attack versus radical coupling mechanisms. An important method mentioned in this Forum Article should be noted: ref 9 is a novel constrained DFT approach by the lead author to limit the impact of the self-interaction error that is present and can affect the results of DFT calculations.

In the second contribution by Solis and Hammes-Schiffer,[10] the focus is on proton-coupled electron transfer (PCET) in electrocatalysis, with emphasis on dihydrogen evolution and reduction. The authors give a pedagogical presentation on calculation of the reduction potentials and pK_A's and their coupling through Pourbaix diagrams (Figure 8 in ref 10). Emphasis is placed on calculating the relative (to known references) potentials and pK_A's to ensure cancellation of errors and to maximize accuracy. This Forum Article also considers the kinetic contributions associated with electron transfer, proton transfer, and concerted mechanisms (see also ref 11 for a detailed review on PCET by the lead author). These thermodynamic and kinetic considerations are applied to cobaloxime and nickel-based catalysts, the latter with pendant amines that serve as proton shuttles and model the behavior of hydrogenase enzymes.

The third contribution by Noodleman and colleagues[12] deals directly with the key biological function of proton pumping coupled to the reduction of dioxygen to water by the heme iron−copper active site in cytochrome *c* oxidase. This class of enzymes uses the energy difference of dioxygen reduction relative to cytochrome *c* oxidation to translate protons across a membrane for adenosine triphosphate synthesis. Their model, further developed from their ref 13 and massively illustrated in Figure 3 of that article, is different from most present considerations in the field. The authors evaluate a mechanism where proton pumping occurs directly at the dioxygen reduction site and involves a His ligand at CuB. The energetics are rigorously presented and provide the basis for future experimental evaluation. It should be noted that these calculations require the use of a spin-unrestricted broken-symmetry formalism developed by Noodleman[14,15] that enables DFT calculations to obtain multideterminant character as required by the magnetic coupling of localized spin centers at the iron−copper site.

The last two contributions in the methods portion of this Forum Article focus on the excited states of transition-metal complexes. The article by González and Freitag[16] focuses on charge-transfer excited states and their reactivity. First, a rigorous electronic structure description of $\{RuNO\}^6$ is obtained using the multireference CASPT2 method. The noninnocent nature of this complex is emphasized with ~25% $Ru^{3+}NO^{\bullet}$ character in the dominantly $Ru^{2+}NO^+$ ground state. The results of the CASPT2 calculations are compared to those from time-dependent DFT (TD-DFT) calculations; the latter are considered reasonable and then used for excited-state dynamics calculations. An elegant and insightful presentation is given on trajectory surface-hopping molecular dynamics simulations to describe the photodynamics of NO release by $[Ru(PaPy_3)NO]^{2+}$, a complex studied by Mascharak et al.[17] that has importance for health applications. The calculations give reasonable estimates of NO dissociation, intersystem crossing, and internal conversion rates, summarized in Figure

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10 of this article. This type of "state of the art" excited-state dynamics calculation is also likely to become extremely valuable for new applications in ultrafast spectroscopy that use X-ray free-electron lasers to study excited-state relaxation and dynamics for solar energy conversion.

In the final methodology contribution, Neese and colleagues[18] present calculations that address high-energy X-ray absorption spectroscopy (XAS) with applications to extended materials. L-edge XAS is particularly challenging to calculate from first principles because of the $2p^5 3d^{n+1}$ nature of the final states, which undergo significant valence-core electron repulsion, and a large 2p spin−orbit coupling. This contribution calculates transitions to these states using a restricted open-shell configurational interaction singles method developed by the authors in ref 19, where both Hartree−Fock (HF) and DFT wave functions are evaluated and B3LYP/ROCIS is favored based on correlations to data. These calculations are applied to bulk CaF_2 and TiO_2 and include a systematic evaluation of cluster embedding for long-range effects and hydrogen-capping models. Through an insightful analysis of their calculations, these researchers distinguish local versus extended state contributions to the L-edge spectra of these materials and decompose the L-edge spectral features in terms of major single-electron transition contributions (Figure 13 in this contribution).

In the second part of this *Inorganic Chemistry* Forum issue, the focus is on reactivity and catalysis involving various inorganic species. These papers illustrate how the interplay between theory and experiment advances the level of understanding.

The contribution by Harvey and colleagues[20] describes a computational study of the iconic Fenton reaction between an aqueous ferrous ion and hydrogen peroxide. The potential energy surface (PES) was calculated with various levels of theory, ranging from DFT to explicitly correlated coupled-cluster theory [CCSD(T)-F12]. This study shows that, while previous DFT calculations did not correctly predict this reaction, it is possible to do so, provided one takes into account all of the physics of the system. The authors focus mostly on the chemistry at low pH and show that the free-energy barrier to forming a hydroxyl radical and iron(III) is lower than that for forming an iron(IV) species. These results are consistent with experiment, while previous calculations predicted that iron(IV) formation should dominate. The reason for the success of this study resides in the choice of the functional, B3LYP-D3, which includes dispersion corrections and gives a description similar to that of the benchmark method [CCSD(T)-F12], the use of a large basis set, and the inclusion of relativity and solvation in the model. This study is pedagogical in showing how one should approach the electronic structure theory. The comparison between different methods and the systematic inclusion of various effects, like relativity and solvation, is particularly instructive.

The contribution by Sakaki and colleagues[21] discusses the oxidative addition reactions of the Si−H bond of silane to $Cp_2Zr(C_2H_4)$ and that of the H−H bond of dihydrogen to $Ni[MesB(O\text{-}Ph_2PC_6H_4)_2]$ as examples of the importance of the σ-bond activation of small molecules by transition-metal complexes. Reactions based on σ-bond activation are usually classified into four categories: concerted oxidative addition to the metal center only, stepwise oxidative addition via nucleophilic attack, oxidative addition to M−L (L = neutral ligand), and heterolytic activation by M−X (X = anionic ligand). Experimental examples of these four reactions are presented, and the electronic structures of the species involved are analyzed based on theoretical studies.

The contribution by Eisenstein and colleagues[22] describes the study of the homogeneous reduction of pyridine to piperidine mediated by $[1,2,4\text{-}(Me_3C)_3C_5H_2]_2Ce(\eta^2\text{-}NC_5H_4)$ and dihydrogen. The synthetic, spectroscopic, and computational results are reported. Theory, in this case, was employed to identify the possible pathways of hydrogenation. The important finding that emerged from the computational characterization is that the mechanism involves both an intra- and intermolecular step, and the intermolecular step is responsible for the productive hydrogenation of pyridine. It is interesting to note that these calculations would have not been possible 20 years ago because the computer power and codes available then limited the calculations to only a small model of ligands. Today, full calculations are affordable because of the further development of computational methods and the advances in computational resources.

In the contribution by Frenking and colleagues,[23] the calculated profiles for four reactions of small molecules with amidoditetrylynes $R_2N\text{−}EE\text{−}NR_2$ (E = Si, Ge, Sn) are reported. This study is a nice example of how the interplay between theory and experiment enables the advancement of science. The agreement between the experimental and computed results illustrates a good validation of the theoretical models, although when a discrepancy between theory and experiment occurs, as in one of the hydrogenation reactions, the authors explore the possible reasons for this and test different models. The computational study improves the understanding of the details of the reactions and inspires future experiments, which can focus on more promising systems.

The paper by Lehnert and colleagues[24] reports the results of a combined experimental and computational study on $\{[Fe(OEP)]_2(\mu\text{-}N_2O_2)\}$, a model complex of the diiron heme/nonheme active site of bacterial NO reductase. Analysis of the electronic structure and reactivity of the model complex provides further insight into alternative mechanisms of reductive N−N coupling that are chemically more feasible than the existing models. For this purpose, a combination of magnetic circular dichroism, nuclear resonance vibrational spectroscopy, magnetic measurements, and DFT calculations is presented. The DFT calculations were performed to assign the vibrational features of $\{[Fe(OEP)]_2(\mu\text{-}N_2O_2)\}$ and identify the interesting species involved in the reactivity of this compound. This paper again emphasizes the interplay between theory and experiment.

The majority of the presentations strongly emphasize the application of DFT methods. (Note that the articles by González,[16] Neese,[18] and Harvey[20] and their colleagues also describe the application of wave-function-based methods.) While DFT is largely used, it has limitations based on the single-reference nature of the calculations and the inherent self-interaction error. As presented in the contributions to this Forum issue, these can be minimized by hybrid and constrained functionals and broken-symmetry methods. Alternatively, we thought it would be useful to include the following comments on wave-function-based multireference computational methods. Additionally, because all presentations emphasize the calculations and their use in understanding inorganic chemistry, we thought it useful to include comments on using spectroscopies to evaluate the accuracy of quantum calculations.

QUANTUM-CHEMICAL METHODS FOR SPECTROSCOPY AND REACTIVITY

One of the challenges for modern quantum-chemical methods is to accurately describe multiconfigurational systems, that is, systems whose electronic structure cannot be represented in a good approximation with a single way of distributing the electrons in the orbitals. More technically, they cannot be described with a single-configurational wave function. Such systems are usually labeled as "strongly correlated" or "multireference" systems. Examples of inherently multiconfigurational chemical problems include bond breaking,[25] PES degeneracies (conical and glancing intersections),[26] symmetry-breaking problems,[27] biradicals,[28,29] organic photophysics,[30−33] transition-metal multiple bonding[34−39] and spectroscopy,[40−42] and actinide chemistry.[43,44] Of special relevance here is the treatment of reactivity and properties of the ground and excited electronic states of systems containing transition metals.

In Kohn−Sham density functional theory (KS-DFT),[45−47] the spin densities are represented by a single-configurational wave function, the Slater determinant. For multiconfigurational cases, the accuracy in the energy obtained with the existing functionals is typically low.[48−50] Therefore, one of the unmet challenges for DFT is the proper treatment of multireference systems and, more generally, the treatment of nearly degenerate states. Multiconfigurational methods,[51−63] on the other hand, are able to treat near-degeneracies with no ambiguity.

CORRELATIONS OF EXPERIMENT TO CALCULATIONS

The methods summarized above computationally evaluate the electronic structure. The descriptions that these generate quantitatively vary depending on the level of calculation. Spectroscopic methods quantitatively determine the electronic structure experimentally, enabling evaluation of the accuracy of the above calculations. Calculations supported by spectroscopic data provide further insight into reactivity via frontier molecular orbitals and the reaction coordinates they define.

The traditional methods for evaluating the covalency of metal−ligand bonds in transition-metal complexes, defined here as the amount of ligand character mixed into the valence d orbitals, mostly focus on electron paramagnetic resonance (EPR) spectroscopy. The most direct experimental probe from EPR and related spectroscopies [i.e., electron nuclear double resonance (ENDOR) and electron spin-echo envelope modulation (ESEEM)] of the covalency of the ligand−metal bond is the superhyperfine coupling of the ligand nuclear spin to the electron spin. This is dominated by covalent delocalization of the electron spin density into the ligand hybrid orbital involved in bonding to the metal center. Alternatively, experimental methods to quantify the covalency of ligand−metal bonds using synchrotron radiation are now available that involve XAS at different metal and ligand edges.[64,65]

It is important to finally note that calculations that give good agreement with experimental probes of covalency also agree well in their correlations to a range of spectral features (e.g., from TD-DFT), structures, and energetics and provide fundamental insight into the physical properties and reactivity. This interplay between theory and experiment is a key theme of this *Inorganic Chemistry* Forum issue and is emphasized by the 10 invited contributions from major researchers in this field.

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