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A Tribute to Sason Shaik[†]

It is a pleasure and honor for us to introduce a special issue dedicated to the scientific achievements of our mentor, guide and former supervisor, Professor Sason S. Shaik. Although the official date of birth of Sason has been lost in history, it is predicted that his 60th birthday will commence somewhere in 2008. We thought this would be the ideal time to celebrate his birthday with a special issue in the *Journal of Physical Chemistry* dedicated to his broad and exceptional accomplishments to the Physical, Organic and Bioinorganic Chemistry communities. We are delighted that the Editorial Board of the *Journal of Physical Chemistry* has approved this and thank them for the opportunity this has given us to acknowledge the work of Sason together with a long list of former and present co-workers as well as many scientific friends.

During his already highly successful and fruitful scientific career, which we hope will continue for many more years to come, Sason put a firm stamp on theoretical chemistry and functioned as an ambassador of the field toward the general science community. Thus, although theoreticians often work on fundamental problems, with sometimes-limited practical value, Sason has always tried to make the work accessible to a large general audience. This, for instance, has resulted in (co)-authorship of 93 publications in the *Journal of the American Chemical Society* (at the time of writing of this Tribute). Consequently, his work has influenced not only theoretical chemists, but also inorganic-, organic-, and biochemists (among many others). This influence is also reflected in the broad range of contributions, which this special issue has attracted, from authors with a wide spectrum of backgrounds ranging from experimental biochemists and inorganic chemists to mass spectrometrists, physical chemists and, of course, theoretical chemists and physicists.

In this short Tribute it is impossible to describe all scientific achievements and breakthroughs of Sason in detail. We have therefore chosen to focus on a few key highlights that have established him as a world leader in his field.

Valence Bond Modeling

Sason's earliest successes are associated with valence bond (VB) modeling of reaction processes. During his Ph.D. with Nicholaos D. Epiotis, he "discovered" this largely forgotten theory and had a short flirt with it. Subsequently, during his postdoctoral period with Roald Hoffman, he saw the benefit

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[†] The former name used in publication is Sason S. Shaik.

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of using both localized and delocalized electronic structures and developed the technical means to project molecular orbital (MO) wave function with or without configuration interaction (CI) into VB structures, based on fragment orbitals or atomic hybrid orbital, as deemed necessary for the particular problem. At that time, the VB methodology was out of fashion and only a few people in the world were actively engaged in the use of its techniques. Sason immediately recognized the potential of this theory to describe basic reaction mechanisms in a simple and straightforward way. Mainly thanks to his and his many co-workers' tremendous efforts in the field, the VB methodology has survived and is gaining interest and momentum ever again.

He applied the VB technique to explain and predict reaction mechanisms of polar reactions, electron transfer processes, cycloadditions and many bond reactions.[1] Thus, it was shown that an elementary reaction from reactants to products can be described with a curve crossing diagram, whereby the avoided crossing provides the transition state of the reaction, and an important excited state surface that is crucial for the photochemical transformation. It can be shown, therefore, that the wave function in the transition state is a mixed VB wave function of reactants and products. The work on VB modeling has been done in collaboration, initially with Pross, and later with the Hiberty and Wu groups. The tools developed by Sason and co-workers have given great understanding of basic reaction mechanisms in organic and inorganic chemistry.

Two-State Reactivity

In the mid 1990s, Sason Shaik and Helmut Schwarz of the Technical University of Berlin (Germany) began a collaborative project on gas phase reactions of transition-metal-oxo species. The mass spectrometric studies of the Schwarz group produced conflicting results and a model was needed to explain the reaction mechanisms and observed rate constants. A collaborative project of the two groups resulted in the hypothesis of two-state-reactivity (TSR), whereby an active oxidant has an electronic ground state with two close lying spin states.[2] It was predicted that the oxidant would be able to react with substrates on both spin state surfaces that would give different rate constants and different products on each spin state surface. This seminal discovery of Shaik and Schwarz et al. was later shown to be common in transition metal containing oxides.[3] In particular, it explained the reactivity patterns of a key enzyme for human health, the cytochromes P450, whereby the active form is an iron(IV)−oxo heme(+•) called Compound I.[4] Thus, Compound I is described as a triradical species, with two electrons in orthogonal π^*_{FeO} orbitals and a third one located on a heme orbital called a_{2u}. It was shown that ferromagnetic coupling of these three orbitals gives a quartet spin state, whereas the antiferromagnetic coupling gives a doublet spin state. The quartet and doublet spin states of Compound I of P450 enzymes are close in energy and, as a consequence, give rise to different reaction barriers on each spin state surface. This has been termed two-state-reactivity (TSR) and explains the experimentally observed product distributions and kinetic isotope effects. These scientific discoveries have set the scene for many future projects in the Shaik group and focused on the elucidation of reaction mechanisms of short-lived oxidants in enzymatic systems. Sason was one of the first people to realize that a challenging system like the cytochromes P450 needed more advanced methods and techniques than the commonly used model calculations on extracts of enzyme active sites. In collaboration with Walter Thiel from the Max Planck Institut für Kohlenforschung in Mülheim an der Ruhr, the two groups started working with quantum mechanics/molecular mechanics (QM/MM) techniques. Indeed, for the complicated description of the electronic ground state of Compound I of cytochrome P450, for instance, it was quickly seen that the protein environment added a crucial perturbation to the model that influenced the electronic properties of the metal center considerably. In the past six years or so, the QM/MM methodology has been further developed and optimized for many transition metal containing systems. The work has given tremendous insight into fast processes that happen in enzymes and have led to many predictions for experimental studies, such as the elucidation of reaction mechanisms, the identification of the active oxidant in the reaction process and the origins of byproducts.

Bonding

The most recent seminal contribution of Sason Shaik we highlight is his work on bonding, charge-shift bonds and ferromagnetic bonds. Especially intriguing are the ferromagnetic bonds, which bind atoms without any electron pairing. Thus, calculations on alkali metal dimers in a triplet spin state ($^3Li_2$, $^3Na_2$ etc.) showed that these clusters are stable albeit with a small bonding energy.[5] This is quite surprising because $^3Li_2$ has only one electron in a σ-bonding type orbital but another one in a σ^*-antibonding orbital, which should make the system dissociative. The work of Shaik et al., however, showed that despite the fact that these systems lack bonding electron pairs they are stable clusters due to ferromagnetic coupling of electrons in the maximum spin state. Thus, it was shown through valence bond modeling that the ferromagnetic bonding comprises delocalized covalent-ionic fluctuations that spread over and bind the high-spin cluster. The bonding energy per atom in a cluster increases and converges to a limiting value, at around 10−12 atoms. This ferromagnetic bonding is particularly large for lithium and copper clusters and decreased for elements down the periodic table.

Summary

The previous three sections only highlight three major contributions of Sason to science in general, which represent only a fraction of the actual work he has done. Despite the fact that Sason always has had a modest size research group with limited resources, he has been doing exceptional high-quality research and made major scientific contributions. We are proud and honored to have had the opportunity to work with him for several years. He has been a fantastic supervisor. It should be mentioned here that he is very demanding and precise, but he demands the same of himself, all in the pursuit of the best possible science. We all remember the numerous hours he spent with us to explain a concept. Redrawing Figures for publications a couple of dozen times until perfection is one of the things you will have to get used to when you work for Sason, but in hind-side these modifications always improved the quality of the work. We have learnt very much from his guidance and working style and congratulate him again with this Special Issue and hope readers will enjoy the contributions.

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Sam P. de Visser
The University of Manchester

Etienne Derat
Université Pierre et Marie Curie

Devesh Kumar
Max-Planck-Institut für Kohlenforschung

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