

BOOK REVIEWS

Annual Review of Physical Chemistry, Vol. 67. Mark A. Johnson and Todd J. Martínez (eds). Annual Reviews, 4139 El Camino Way, P.O. Box 10139, Palo Alto, California 94303-0139, USA. 2016. ix + 765 pages. Price: US\$ 102.

This volume of the *Annual Reviews of Physical Chemistry (ARPC67)* once again brings out the sheer breadth of contemporary physical chemistry research. The so-called ‘middle kingdom’ is indeed rather vast – as is eminently clear from the various articles that range from processes happening inside a cell to tracking the motion of electrons. *ARPC67* has a good balance between theory and experiments, applied and fundamental, representing frontline research on gas, condensed and solid phase systems. As always, it is good to hear from the masters talking about their research journey with all the trials and tribulations that they faced – precious information for young scientists starting their research careers. The prefatory article by Giacinto Scoles is enjoyable to read. From his unique perspective on teaching to having the famous ‘bolometer paper’ being rejected by *Journal of Chemical Physics*, Scoles’ article is brutally honest. Interestingly, his reaction of what ails the Italian university system can very well be applied to the Indian university system as well.

Gas phase reaction dynamics has been at the core of physical chemistry for nearly a century. From the early formulations of transition state theory to the advances in quantum reactive scattering theory, numerous experimental and theoretical studies have led to tremendous insights into the interplay between structure and dynamics. However, it is only recently that experiments and theory have become sophisticated enough to test the veracity of the several hypotheses, thumb rules and models for reactivity that have been around since early times. Consequently, studies continue to reveal intriguing results even in, what were thought to be, well-established reactions. *ARPC67* highlights a few of the areas wherein the results challenge, and provide a fresh perspective on the traditionally held viewpoints. Kopin Liu’s review of the recent progress in our understanding of mode and bond-specific reactivity indicates, apart from shedding new light on the old Polanyi rules, that the ‘dream

is still alive’. Remarkably, Liu concludes by saying that ‘our present understanding about the vibrationally induced dynamics of polyatomic molecules barely scratches the surface’, and I concur. Seemingly, one would have to address the problem of tracking the energy flow during a reaction in some detail. In other words, one can no longer afford to wish away the notorious intramolecular vibrational energy redistribution (IVR) phenomenon. In fact, issues pertaining to IVR crop up again in the review of the state-of-the-art quantum scattering studies by Zhang and Guo. This review nicely complements the one by Liu and demonstrates the impressive accuracy that can be achieved in computing the cross-sections to capturing the ephemeral resonances. Not only do such exact quantum dynamical calculations provide us with a wealth of data, they also help, by comparing to the quasiclassical results, delineate the quantum effects that come into play in reactive scattering. Tesa-Serrate *et al.* take the scattering experiments to another level and reveal as to how colliding gaseous atoms and molecules with liquid surfaces can tell us about the nature of the gas-liquid interfaces. Interestingly, models like the hard-sphere binary collision model that were formulated in the context of gas-phase scattering are still capable of yielding qualitative insights. The complexity of the collisions at a liquid surface in terms of reactive events is summarized nicely in figure 8 of the review. Consequently, the challenges for theoreticians is substantial and, as stated in the conclusion by the reviewers, experiments lead theory by a large margin in this area of research.

Speaking of reactions and their underlying dynamics, one cannot but help wonder whether the infamous issue of identifying the appropriate reaction coordinate has been finally resolved. Infamous since this issue was raised and hotly debated in the seminal Faraday discussions on transition state theory in 1938. Also of interest is the way, and how often, that the molecules get to the transition state. Indeed, most chemical reactions are examples of rare events and sampling rare trajectories poses quite a challenge for reactions in multidimensional systems. Two reviews in *ARPC67* are dedicated to this key topic. The first one by Valsson *et al.* reviews the powerful approach of metadynamics for sampling rare events. The authors emphasize

the need for a good starting guess for the so-called collective variables and provide a brief summary of the various avatars of metadynamics to obtain a converged free energy surface. The discussion in the section titled ‘A recipe for selecting good collective variables’ should provide a clue to the reader as to why the 75-year-old issue still troubles us. Baron Peters, on the other hand, does not mince any words and starts his review by asking whether ‘reaction coordinates are unnecessary, convenient, or crucial’ and ends the review by stating that ‘Human intuition remains the best source of trial coordinates and mechanistic hypotheses, and there is no procedure for having an epiphany’. That pretty much sums up the reason that we pchemists are still in business. I wonder if that is also a strike against the so-called machine-learning approaches.

The appearance, or disappearance, of dynamical complexities as one goes from single molecules to clusters to extended systems embedded in their natural environments, is of great interest from the viewpoint of establishing universal trends. Stavros and Verlet bring out the utility of a firm understanding of the gas-phase dynamics, using techniques that are also employed in the studies highlighted by Liu as well as in order to appreciate the influence of the ‘environment’. So, is the observed ${}^1\pi\pi^*/{}^1\pi\sigma^*$ conical intersection in imidazole relevant for the dynamics of adenine? Should one expect it to be relevant for adenine in the aqueous medium? This bottom-up approach to the ultrafast dynamics in complex systems like the oligonucleotides has its advantages and drawbacks. Stavros and Verlet make a strong case for more such experiments in order to unambiguously correlate structure and dynamics of complex biomolecules. The review by Kostko *et al.* highlights the experimental advances in understanding the photoionization of various types of molecular clusters using tunable vacuum ultraviolet light sources. It is fascinating to see the amount of rich information that one can obtain by exciting the valence electrons. At the same time, these experiments are providing quite some challenge to theoreticians, both in terms of accurate calculations as well as coming up with appropriate models. There is no doubt that such a bottom-up approach should be complemented with top-down approaches as well. Since, it is only then that,

hopefully, a clean dissection can be made of the complex dynamics into contributions due to the environment and effects intrinsic to the system; thereby establishing the usefulness of the paradigmatic ‘system-plus-bath’ model. However, performing experiments in the context of the top-down approach is challenging and one needs to carefully chart out the valence electronic energies in aqueous environments. Seidel *et al.* show how one can extend the photoelectron spectroscopy (PE) technique to the aqueous phase with the exciting possibility of being able to determine solvent reorganization energies and standard reduction potentials. Apart from discussing the aqueous PE spectra of halide and transition metal ions, the problem of determining electron binding energies of biomolecules in their native environment is also highlighted. Interestingly, and related to the article by Stavros and Verlet, there are indications that the lower vertical ionization energies of the nucleobases are insensitive to the environment. This magical outcome is due to the remarkable screening effect of water.

The transition from understanding the influence of the various electronic states on the dynamics of a complex system to probing the dynamics of the electrons themselves, is an exciting prospect. Catching the electron in the act, as one might say, is like listening to the heartbeat of chemistry. Feeling the pulse of the electron, however, needs really fast pulses – attosecond, that is. The review by Ramasesha *et al.* summarizes the amazing advances made in attosecond spectroscopy to understand the mechanism of ultrafast charge migration in molecules to following the transport of electrons on solid surfaces. The possibility of a deeper understanding of non Born–Oppenheimer dynamics and electron correlations is certainly tantalizing. It is also of some interest to examine if the techniques can be used to gain insights into charge transfer/carrier dynamics in more complex systems. Several reviews in *ARPC67* bring out the complex charge dynamics in a variety of systems. Herz highlights the key aspects of charge-carrier dynamics in a class of perovskites, whereas Zhu *et al.* discuss the charge transfer dynamics in semiconductor quantum dots. The role of charge transfer states in organic thin films is brought out clearly in the review by Vandewal. These articles highlight the

challenges inherent to fabricating devices that utilize the important role, in terms of timescales, competing processes and energetics, of the charge carriers. One thing is for sure – the sheer number and complexity of the processes that happen in such devices are daunting, and extracting even coarse guidelines for making significantly efficient devices will keep this field of research active for some time to come.

The phenomenon of IVR, mentioned earlier, has been appreciated to be a crucial factor in reaction rate theories for more than a century. A naive viewpoint is that distinguished IVR pathways will cease to exist as the system becomes larger. Ironically, with the advent of nano- and mesoscale systems as the focus for designing materials with novel properties, specific energy flow pathways are crucial once again. In fact, characterizing both intra- and intermolecular energy flow in such systems is becoming mandatory. Three reviews in this volume address/use the energy-flow phenomenon in varied situations. Segal and Agarwalla provide a nice account of the IVR that occurs in molecular nanoscale junctions. One can appreciate the need for building simple, but relevant models to account for anharmonicity, reservoirs and impurities. ‘Gluing’ together the various models to capture the heat transport in real systems is an outstanding challenge. For instance, although not the focus of the review, does the usual Fourier heat law hold in such molecular junctions? The phenomenon of electronic energy transfer from one chromophore to another has been a workhorse for researchers ever since Förster introduced the idea in 1948. Holmstrom and Nesbitt review the recent advances made to the Förster resonance energy transfer (FRET) technique. More precisely, they beautifully illustrate the power of combining single-molecule FRET with external temperature control to extract important physical parameters like the entropy and enthalpy change associated with conformational equilibrium of a complex biomolecule. It is indeed satisfying to see the single-molecule FRET being connected to the Van’t Hoff and Eyring equations. ‘Thermodynamics measurements at a single molecule level’ – now there is a concept that is worth discussing in a pchem class. Such experiments can map out the free-energy surfaces of rather complex systems and will surely provide enough

challenges to the rare event sampling community. In fact, as discussed in Yu’s review, single-molecule techniques have now been ported over to studying dynamical processes occurring in live cells. However, accurately capturing the heterogeneity of the cellular environment using the stochastic single molecule datasets needs careful statistical analysis. Yu provides a clear description of the various statistical models which go beyond the simple mean squared displacement sort of analysis. The intracellular environment is quite rich and gives rise to dynamical effects that challenge a simplistic Gaussian diffusion model. Speaking of chromophores and energy transfers, one cannot but help think about the photosynthetic systems. It has been nearly a decade since Engel *et al.* espoused the surprising viewpoint that quantum electronic coherences can survive at physiological temperatures. This hotly contested and much debated work has resulted in a tsunami of activities with every aspect being checked at unprecedented levels of detail. Theorists who had till then been in the comfort zone of relying on the temperature washing away quantum coherences and using model spectral densities were suddenly made uncomfortable. Lee *et al.* review the semiclassical path integral dynamics approach to understanding the photosynthetic energy transfer. As noted by them, and emphasized several times by Bill Miller, the act of putting both electronic and nuclear degrees of freedom on the same dynamical footing is crucial – parametrized one-size-fits-all molecular mechanics force fields are not appropriate. Coming from the Miller school, I can see why; if one is out to understand long-time coherences, which involve both electronic and nuclear degrees of freedom, then we need \hbar throughout and consistently – cannot afford to make one part classical and another part quantum. The results for the FMO complex shown in figure 5 of the review by Lee *et al.* underline the danger of underestimating the bath dynamics. Reminds me of the classic paper by Oxtoby and Rice (*J. Chem. Phys.*, 1976, **65**, 1676) wherein they conclude that ‘the form of the memory function must be rooted in dynamics and should be defined in terms of molecular properties’. Here is something to think about for all those studies wherein researchers use a ‘vanilla form’ of spectral density: are they missing out on

interesting dynamical phenomena? Can one shoehorn the results of a simulation to the model spectral densities? Should one?

Many reviews in *ARPC67* are concerned with advances in spectroscopy – our eyes into the rich and dazzling world of atoms and molecules, and of their structure and dynamics. Two-dimensional spectroscopies, vibrational and electronic, have emerged as the key tool for the past few decades. In this volume, Reppert and Tokmakoff focus on computational aspects of 2D IR spectroscopy of the amide-I group in proteins, because of the large transition dipole moment. Teasing out the intrinsic features of proteins that makes them special requires close partnership between theory and experiments. And, as pointed out by Reppert and Tokmakoff, imperfect force fields are just one of the niggling worries. Non-linear spectroscopies are becoming increasingly important in order to measure and characterize phenomena that are otherwise elusive. For instance, insights into the interfacial structure and dynamics has come from the extensive use of various nonlinear spectroscopic techniques. Covert and Hore discuss the applications to geochemistry in terms of probing the mineral-water interfacial structure and understanding the phenomenon of dissolution. Their figure 4 stresses on an important issue – understanding natural interfacial systems needs to include the flow characteristics. One may even infer the wrong surface charges (both sign and magnitude!) with studies based on stagnant interfaces. The review by Covert and Hore is a good example of the wide-ranging applications for a technique that was once thought to be only of fundamental relevance. Understandably, the theoretical underpinnings of nonlinear spectroscopy are of considerable interest, and Chulhai *et al.* provide a rather detailed review in the context of surface-enhanced vibrational spectroscopies. The differences between signal enhancements due to electromagnetic mechanism and chemical mechanism are explained within a single theoretical framework. This review should be a valuable resource for researchers working on characterizing molecules adsorbed on metal nanoparticles. Interestingly, several reviews in *ARPC67* address issues pertinent to nanomaterials in terms of accurate determination of their size, nature of the localized excitations and their use in bio-

sensing. Cherqui *et al.* highlight the advantages of using a nonoptical approach, the electron energy-loss spectroscopy (EELS) method, for understanding localized surface plasmon resonances. Apart from a succinct introduction to the theory of EELS, one can find a clear discussion of competing energy transfer mechanisms and quantum effects arising from the quantumness of the electron as well as of the photons. Dominguez-Medina *et al.* address the important problem of ‘sizing up’ the colloidal nanoparticles and show how the fluctuation correlation spectroscopic technique can help in this regard. It is interesting to see as to how one can infer the interaction between nanoparticle aggregates and proteins using diffusion measurements. Hahn focuses on the unique optical properties of ZnO nanorods that make them particularly attractive for use as biosensors. The versatility of the ZnO nanorods is quite amazing and it is gratifying to see that much of these properties has been obtained from many different spectroscopic techniques, some of which are reviewed in this volume. However, it is sobering to note that despite a large number of studies, the path to a real-world laboratory-scale sensor is still a challenge. As a note, understanding the various plots in figure 3 with the provided caption proved a bit challenging. Liao and Zheng’s review sheds light on how one can track the transformations that nanoparticles undergo in liquid medium. The tool of choice here is transmission electron microscopy (TEM) on samples confined to a liquid cell. Thus, one can actually track the growth of a nanoparticle aggregate and hence uncover mechanistic insights that are difficult to infer otherwise. Several other processes like the onset of corrosion and imaging of cells are amenable to this powerful technique.

It is tempting to think of the enormous insights that can be gained into phenomenological rate theories like Kramers or Grote–Hynes, if one could ultimately use the liquid cell TEM technique to probe the transition state of a reaction in solution. Nevertheless, a microscopic understanding of reactive processes in solutions itself poses several interesting challenges. Foremost among them is to dissect the solute–solvent interactions and, in the context of aqueous solutions, a clear understanding of the phenomenon of hydrophobicity. Surprisingly, we are

still far from a clear understanding of the hydrophobic effect, as evidenced by the reviews by Hillyer and Gibb, as well as Ben-Amotz. The switch from an entropy-dominated to enthalpy-dominated regime as the shape and size of the solute is changed is brought out beautifully by Hillyer and Gibb. Ben-Amotz provides an overview of the current theoretical understanding of the hydrophobic effect. Fittingly, in the introductory paragraph itself, Ben-Amotz gives a warning that the review ‘upends common misconceptions regarding hydrophobicity’. So, interactions between two nonpolar molecules in the gas phase are far stronger than their interaction in water. These two reviews on hydrophobicity are well written, and the ideas presented need to be communicated to chemistry students very early on in their education.

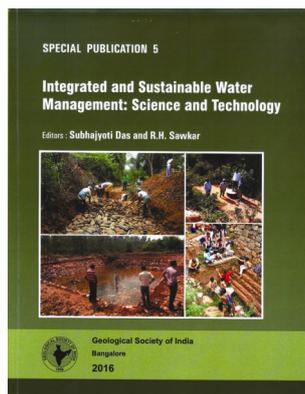
Four of the reviews in *ARPC67* are exclusively concerned with advances in theoretical chemistry, both structure and dynamics. Subotnik *et al.* provide a illuminating discussion on a semiclassical perspective of nonadiabatic effects and dynamics on multiple electronic surfaces. Tully’s surface hopping algorithm, proposed quarter of a century ago, has been particularly popular since doing fully quantum dynamical calculations for a long time is computationally demanding. Subotnik *et al.* give a clear introduction to Tully’s method and bring out the key drawbacks. Apart from the clarity of the article, and hence an essential read for researchers interested in non-adiabatic dynamics, one cannot but resist the beauty of a semiclassical perspective yielding physical insights into a rather complex phenomenon. The review by McDaniel and Schmidt concentrates on an important aspect – calculation of accurate force fields from first principles. Given that accurate force fields are central to any dynamical study, it is hard to understate the importance of this review which focuses on using symmetry information to obtain force fields. The details presented in table 1 is informative and it is impressive to see less than a kcal/mol error for noncovalent interactions. However, it seems like integrating such accurate force fields into the black-box molecular dynamics simulation packages is still a distant dream. The review by Danovich and Shaik details a novel bonding that arises in metal clusters, but without the need for electron-pairing. This so-called no-pair ferromagnetic bonding is an

example of the ever-expanding notion of a chemical bond, and the high spin metal clusters are expected to play a fundamental role in cold atom chemistry and spintronics. It is refreshing to see the valence bond approach to such novel high-spin clusters. Kronik and Neaton show the power of many-body perturbation theory and density function theory in calculating properties of molecular solids. Such approaches, although computationally demanding, are required for an understanding of the optical properties of organic molecular crystals held together by weak forces. The accurate description of several phenomena that is required to have predictive power is clear from the discussion in the review. Makes one wonder as to how lucky a 'mix and wait' approach needs to be to hit upon the right material.

Thus, in summary *ARPC67* brings out the role of physical chemistry in a wide range of phenomena that span all the way from small clusters to live cells. This is a rather long review of a collection of reviews in physical chemistry. However, for a volume that has 30 articles that span about 700 pages, one cannot hope to do justice in a page or so. I am glad to have glanced through this volume, for several of the articles have been educative and, more importantly, have once again made it clear that challenges abound when it comes to understanding the structure and dynamics of all systems, large and small. I wonder if these diverse sets of topics can be communicated to the students in some fashion so that they get a perspective of this sheer breadth and amazing versatility of the field of physical chemistry.

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Integrated and Sustainable Water Management: Science and Technology. Subhajyoti Das and R. H. Sawkar (eds). Geological Society of India, No. 63, 12th Cross, Basappa Layout, Bengaluru 560 019, 2016. xviii + 196 pages. Price: Rs 1500.

Water is a key factor in sustainable development of a nation. Hence, the status of water resources and their sustainability, particularly in the arid and semi-arid areas of the country, are of prime concern. Rainfall, the source of all water on earth, has a huge spatial and temporal variation in the Indian subcontinent; it is mainly confined to four months during the monsoon season in a year. India has nearly 33% of its geographical area in the semi-arid and arid category. A substantial part of the arid and semi-arid areas is drought-prone.

Although agriculture is the backbone of our economy, 65% of the net arable area of the country is rainfed and contributes to about 45% of the total food-grains production in the country. No development is possible without food and drinking water security. Uncertainties in rainfall and uneven water resource availability in space and time are the major constraints in socio-economic development of the region.

Groundwater is the all-important source for drinking water and agriculture in the peninsular region of the country. However, a major part of this terrain is underlain by consolidated formations like granites, gneisses, trappean basalts, metamorphics and cemented sedimentary rocks that hold a moderate to limited reserve of groundwater in the weathered residuum and fractured-rock aquifers, susceptible to overexploitation leading to chronic water scarcity.

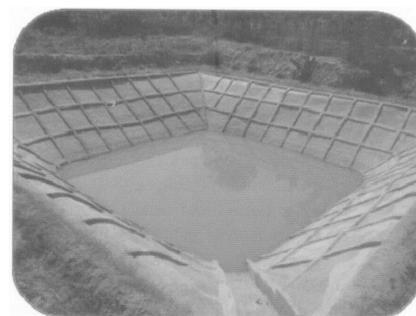
This book encompasses 23 peer-reviewed research papers organized in two

sections, namely 'Integrated water management and people's participation'; and 'Science and technology in water conservation'.

In the first section, vital issues regarding water management such as the integrated water resources management, water sustainability, water equity, planning and water reforms, water use efficiency, urban water management, inter-basin water transfer, public participation and involvement of citizens, etc. have been discussed.

Aquifer mapping is an important step in aquifer management for sustainable groundwater management. A robust community-based approach for this common pool resource is necessary and to that end, the policy of 'know your aquifer, manage your aquifer' has been advocated. The significance and scope of large-scale rainwater harvesting and artificial recharge in the drought-prone areas of the country have been explained to find a solution to the falling groundwater level and as supply-side management. Importance of soil moisture and water conservation, crop-water planning, irrigation efficiency and rainfed agriculture on demand-side management has been discussed at length.

The importance and effectiveness of people's participation in the management of groundwater resource have been illustrated through interesting case studies and analyses in the book. A few case histories of successful water harvesting and conservation efforts with community participation in the Aravari basin in Rajasthan and Ichalahalla, Kumudvathy and Vedavathy watersheds in Karnataka have been discussed in detail. This has brought out the importance of integrated watershed management based on indigenous knowledge systems with modern inputs for all-inclusive rural growth.



Farm pond for *ex situ* rain water harvesting.