

BOOK REVIEWS

Annual Review of Physical Chemistry, 2009. Stephen R. Leone *et al.* (eds). Annual Reviews Inc., 4139 El Camino Way, P.O. Box 10139, Palo Alto, California 94303-0139, USA. Vol. 60. xii + 524 pp.

As soon as *Current Science* approached me to review the latest *Annual Review of Physical Chemistry (ARPC)* I gladly accepted. After all, this was my chance to catch up to some of the exciting advances in my broad field of interest. Moreover, and I am not ashamed to admit, getting a free copy of the latest *ARPC* was very enticing – even as a graduate student in the early 1990s in the US, it was not easy to afford a personal copy of the book. As I started to read the various chapters written by the experts, a question constantly cropped up: ‘How, and perhaps why, should one at all review a collection of reviews?’. More so since the preface by the editorial team of *ARPC* already puts the volume and contributions in perspective. And then I came across a fascinating article (*Ann. Intern. Med.*, 1987, **106**, 485) by Murlow on what makes an ideal review. The focus was on medical review articles but her statement – ‘Good review articles are precious commodities. In this era of plentiful and burgeoning medical literature, the individual’s capacity to read and absorb information has not changed. Reduction of large quantities of information into palatable pieces is essential for digestion.’ – is equally applicable to a review in any field today. Murlow finishes her article by pointing out several criteria for judging the quality of a review. Two of the criteria are particularly important: First, a well-conceived review always answers a precisely formulated question which is clearly stated at the beginning. Second, gaps in the present knowledge and unsolved issues should be identified and future initiatives should be suggested. Thus the reader finishes the review with a view of what is not known about the subject as well as what is known. If we combine Murlow’s criteria with the suggestion by *ARPC* that the articles should be a valuable resource for graduate and undergraduate courses, then we end up with rather exacting standards for the articles published in *ARPC*! Happily enough, most of the articles in the current volume measure up to the standards.

The current volume reinforces a personal viewpoint that I, and perhaps many

of my colleagues, have had for several years – interesting and challenging questions, pertaining to structure and dynamics, which still remain unanswered in seemingly simple gas phase molecules as well as in apparently complex systems like liquids and biomolecules. Thus, it was gratifying to see that the 24 articles cover the entire range from photodissociation of nitric oxide dimer to the shape changes and movement of a cell. Even more impressive is the fact that physical chemistry can shed light and lead to quantitative insights into such exciting open problems. At the same time the vastness of it all is a humbling experience. Fortunately, the style of presentation and the new format of *ARPC* go a long way in helping readers to navigate this vast yet rich and fascinating terrain of physical chemistry. For instance, highlighting specific references at the end via side notes is a great aid to anyone planning to embark on research in that specific field. However, some authors choose not to exercise this option, perhaps to avoid prejudicing a beginner.

The volume starts with John Waugh’s autobiographical essay ‘Sixty years of nuclear moments’ in which the author, among the pioneers of nuclear magnetic resonance (NMR) spectroscopy, takes us on his half a century long journey through the NMR landscape. The essay is written beautifully and some of the comments clearly bring out Waugh’s sense of humour. For example, he says ‘I now know that professors are supposed to be established authorities on the subjects of their students’ theses. However neither Yost nor anyone in Caltech had any experience with NMR’. Yost was his Ph D advisor! The passage wherein Waugh describes the formation of the Unamerican Chemical Society in response to pressures on him to become a member of ACS so that he might win some of the awards later on is hilarious. Yet, hidden behind that humour is a profound message regarding the ideal scientific temperament that one should have. I was equally amazed that Waugh describes both achievements and failings during his scientific career in a fairly candid manner. So the ‘unforgettable flash during a walk in the garden in 1967’ that led to a breakthrough in high resolution NMR and the discoveries in low temperature NMR that turned out to be ‘interesting curiosities rather than the opening of new technologies’ are recounted with equal passion.

Reading Waugh’s article was even more critical for me since I am involved in teaching (for the first time!) an advanced NMR course this semester. Many times while teaching one tends to forget, unfortunately, that what is now seemingly a routine technique/idea required a brilliant mind for its birth several decades ago. Thus, Waugh’s narration of the circumstances leading to the inception of average Hamiltonians and multiple pulse NMR techniques culminating with the ‘unforgettable flash’ in the garden certainly helped me to put the spin echo lectures in the right perspective. With this beautiful insight into Waugh’s journey as a backdrop, it is quite fitting that the article by Mishkovsky and Frydman describes recent advances wherein ultrafast 2D-NMR spectra are obtained without the use of Fourier transforms. The exciting possibility of real time monitoring of chemical transformations is very nicely illustrated with the examples of the Messenheimer complexation reaction and H/D exchange process in ubiquitin solution. Sensitivity seems to be a major issue of concern in such approaches – clearly, ‘spin choreography’ is still capable of challenging the best!

Spectroscopy and science are inseparable. For physical chemists spectroscopy is the lifeline and hence, unsurprisingly, several articles highlight the awesome advances that let us peek into the innermost secrets of nature. Mike Fayer begins with a review of how 2D infrared vibrational echo chemical exchange spectroscopy can yield valuable insights into ultrafast structural changes in small as well as large molecules. Fayer illustrates the power of the technique with aptly chosen examples. For instance, the *gauche-trans* isomerization of a disubstituted ethane molecule and the fast conformational switching in a myoglobin mutant occur over a timescale of about 40 ps. A particularly intriguing result is summarized in figure 6 of the article wherein the dissociation times of several solute–solvent complexes seem to be determined only by the enthalpy of formation. It is useful to remember that transition state theory would say that the dissociation times should depend on the free energy of activation! Staying with the theme of 2D-spectroscopies, Cheng and Fleming give a illuminating account of the dynamics of light harvesting in the Fenna–Matthews–Olson (FMO) photosynthetic complex. The authors use the

technique of 2D electronic spectroscopy to unravel the complex energy transfer pathways in FMO. Already four years ago, Fleming's group had shown that the excitation energy does not simply cascade stepwise down the energy ladder but seems to follow two main pathways. Now their experiments are hinting towards what Wolynes (*PNAS*, 13 October 2009) calls as 'some quantum weirdness in physiology'; amazingly, the efficient light harvesting in FMO might have to do with persistence of quantum coherence. According to Cheng and Fleming, neither the celebrated Förster nor the sophisticated Redfield theoretical approaches are good enough and one needs to tackle the quantumness head-on (see Ishizaki and Fleming's recent theoretical effort in *PNAS*, 13 October 2009).

Well, if the FMO complex can show its quantumness then what about the molecule of life DNA itself? How does the excess electronic energy in DNA decay and are there preferred pathways in this case as well? These crucial questions are addressed by Middleton *et al.* in their thought-provoking review. I liked the authors' honesty right at the start when they say that 'many of the model systems have limited biological realism'. However, just how valuable such model studies are to the real thing becomes evident on reading the article. The importance of conical intersections and base stacking interactions to the photophysics of DNA, especially the nice summary in figure 7, is brought out very clearly. There is little doubt that detailed experiments on this system are leading to critical questions being asked from the theorists about the mechanism of nonradiative relaxation. Reverse micellar systems are another class of problems wherein hydrogen bonds and vibrational energy relaxation are at the centre stage. Levinger and Swafford provide a critical review of the ultrafast dynamics in reverse micelles, an issue of considerable interest in the context of confined biological systems. The authors emphasize the challenges involved in answering the deceptively simple question – what is the nature of water in the nanoscale hydrophilic core of a reverse micelle? In particular, Levinger and Swafford present a reasonably balanced account of the central debate between two groups: one involved in direct dynamical measurements and the other taking an indirect route using probe molecules as reporters.

The impression that such surprises and challenges are only to be found in proteins is immediately dispensed with upon reading two other excellent reviews by Hanna Reisler and by Birir and Havenith. Reisler presents a very well written account of photofragment spectroscopic methods, with emphasis on the velocity map imaging technique, to gain insights into the dynamics of weakly bound molecules. Reisler's extensive discussion of the gas phase N_2O_4 moiety highlights the point I mentioned earlier. Does the NO dimer behave as a covalently bound molecule or a weakly bound complex? Even for this seemingly simple molecule the answer is that 'it depends'! Later, Reisler discusses the predissociation dynamics of hydrogen-bonded dimers and clearly shows, as in the smaller NO dimer case, the preponderance of state-specific vibrational energy flow patterns. Just as one is recovering from Reisler's account of how a single hydrogen bond can complicate the dynamics, Birir and Havenith up the ante with their exquisite study of the high resolution spectrum of formic acid dimer (FAD) – an eight-membered ring with double hydrogen bonds. Not only is the mechanism of proton transfer, concerted or stepwise, a matter of intense debate but even a theoretical prediction of the ground state tunnelling splitting (experimentally determined by Havenith's group to be $0.0158(4) \text{ cm}^{-1}$ only in 2007) is an outstanding challenge! It is interesting to note that the ground state splitting predictions have ranged from 0.3 cm^{-1} to about 111 cm^{-1} . Incidentally, in what may come as a surprise to many, the first Raman spectrum of FAD was reported in 2007 (Zielke and Suhm, *PCCP*, 9, 4528, in a special issue on molecular recognition!) and ended a 67 year long search for the symmetric inter-monomer stretching mode. Wang and Wang review the advances in photoelectron spectroscopy that yields valuable information about the nature of free multiply charged anions (MCA) in the gas phase. Studying the MCAs in gas phase is highly challenging since they lack the usual solvent stabilization and the coulomb repulsions threatening to tear the molecule apart. However, one can directly measure the excess electron binding energy, probe the repulsive coulomb barrier which results in structures different from the solution phase counterparts and hope to gain insights into the dissociation pathways of charged species. The authors show the

power of combining photoelectron spectroscopy with electron spray ionization technique for generating and characterizing the MCAs. Their figure 9, which shows the low temperature spectra of C_{78}^{2-} and C_{84}^{2-} , illustrates as to how one can gain isomer-specific information on the dianions. The hope is that a very fine understanding of the structure and dynamics of MCAs will emerge by studying them in low-temperature ion traps, and a recent study does that by utilizing a Penning trap (*JACS*, 2009, 131, 9836).

Two other lucidly written reviews demonstrate the power and utility of modern spectroscopy to address environmental issues. For me personally these articles were a joy to read and discover the scientific challenges, as a welcome and much needed change from the political debates on environmental issues, in these fast developing areas. Frank Geiger makes it clear that a quantitative understanding of the processes at surfaces and interfaces in heterogeneous geochemical environments poses a very difficult problem. Despite the complexity, nonlinear optical spectroscopy, akin to a Swiss Army knife, can be used to gain insights at the molecular level. The complexity of the systems is not only clear from the article but also by Geiger's acknowledgement where he says that his students are willing to walk through the walls for him – an enviable position for any advisor to be in! The other article by Sigurbjörnsson, Firanescu and Signorell provides an exceptionally clear account of the subtleties underlying the infrared spectroscopy of aerosols. The article provides a key take-home message – extinction spectra of the aerosols is dependent on the shape and size of the particles. Their figure 3, in particular, very clearly shows that for particles with sizes below 10 nanometres the classical Mie scattering theory is inappropriate and one requires a molecular approach. In addition, one still does not have sufficient insights into the mechanism of homogeneous nucleation of aerosol particles.

Recently, nonlinear optics has become the focus once more as an effective tool to probe molecular chirality. Hauptert and Simpson provide an overview of this field using examples ranging from simple to fairly complicated systems like the collagen polymer. The exciting possibility of measuring dynamical chiral processes in real time is feasible only if one can unambiguously relate the optical

measurements to the absolute molecular chirality. I liked the geometric interpretation presented by the authors for visualizing the relevant tensorial objects.

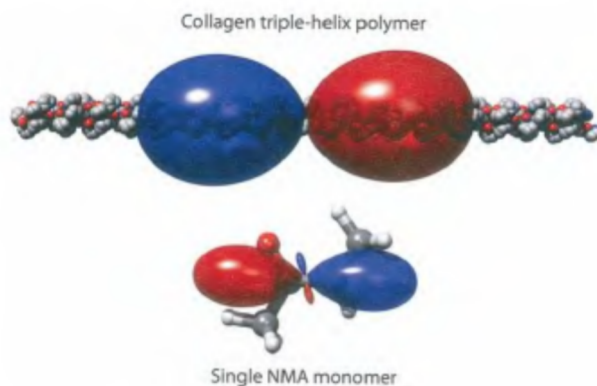
Physical chemistry, as the editorial team mentions, is a discipline that understands elementary systems in great experimental, mathematical and theoretical detail. Surely, out of such detailed understanding must emerge strategies to control the various dynamical processes of interest as well. Attaining this 'holy grail' is not an easy task but over the past couple of decades significant progress has come about due to innovative experiments and novel theoretical approaches. Yaron Silberberg in fact has a different take on this – use ideas from quantum control to improve spectroscopic techniques. For example, quantum control concepts can be utilized to improve the resolution and selectivity of the coherent anti-Stokes Raman spectroscopy. The description of pulse shaping and two-photon absorption are particularly well written. The symbiosis between control and spectroscopy certainly promises to be exciting in the years to come. On the other hand, Rego, Santos and Batista dip into the NMR toolbox and come up with novel techniques to coherently control the quantum dynamics. This article scores high points from a pedagogical viewpoint with its clear exposition of the parallels between multipulse NMR methods and optical control strategies. Control using sequences of unitary phase-kick pulses is discussed using examples of double well tunnelling, decoherence in quantum dots and superexchange electron transfer. In another well-written article, Kenji Ohmori touches upon a subject which relates to the heydays of quantum revolution. In a famous 1926 letter, Lorentz subdued Schrödinger's joy on the discovery of wavepackets and the hope to understand the transition from the micro to the macro world. But he also wrote, 'Nevertheless, if we have to give up wave packets and with them one of the basic ideas of your theory, the transformation of classical mechanics into wave mechanics, something would be lost that would have been very beautiful'. In the current *ARPC*, about 80 years later, Ohmori shows as to how useful the wavepacket idea has proved to be for quantum control. Control by selectively inducing constructive or destructive interference via wavepacket interferometry is indicative of the level of sophistication

that present day experiments can attain. Moreover the exciting development of quantum-state holography, i.e. reconstructing the quantum eigenstate would certainly bring a smile on Schrödinger's face! It is perhaps ironic that one of the first experimental demonstrations of quantum-state holography (Weinacht, Ahn and Bucksbaum, *Phys. Rev. Lett.*, 1998, **80**, 5508) used Rydberg wavepackets.

A very different sort of control is discussed in the article by Lizana *et al.* wherein tiny nanoscale volumes with varying shapes influence the rates and mechanisms of chemical reactions. The authors provide a highly pedagogical review of the field with examples from cell biology and nanofluidics. The central message – standard macroscopic assumptions are violated due to small sizes resulting in efficient mixing due to diffusion and possibility of controlling kinetics by shape and volume changes. I am a bit surprised by the fact that there is no mention of the pioneering work by Gillespie (*J. Phys. Chem.*, 1977, **81**, 2340). The article by Lizana *et al.* is relevant to present day research due to the explosion of activity in engineered nanoscale systems. Two closely related articles, one by Henzie *et al.* and another by Lu *et al.*, describe the making of plasmonic nanostructures by physical and chemical routes respectively. Interestingly, Lu *et al.* adopt a shape-controlled chemical synthetic approach which is nicely illustrated by figure 3 of their article. Henzie *et al.* use soft lithography technique and clearly discuss the importance of shape and geometry on light transmission through the engineered structures. Another article by Walsh and Hersam gives

a clear and readable account of nanoscale patterning with atomic precision using the ultra high vacuum scanning tunneling microscopy approach. All the articles on engineered nanostructures emphasize the key outstanding problem – need for speedy and efficient implementation in order to be technologically viable. Clearly, the challenge is not merely technological and progress can only come from further fundamental studies on surface-molecule interactions. This becomes all the more apparent when one goes through the article by Browne and Feringa wherein they describe the efforts made up until now to engineer smart surfaces that respond to light. Here, there is a need to understand the role of the surface in modifying the photochromic properties of the molecules which are immobilized on the surface. Examples of light-driven opening and closing of nanovalves and light-driven molecular motors illustrate the complexities and challenges involved in this highly interdisciplinary field.

Opinions are divided when it comes to the issue of what sort of insights physical chemistry can provide into biological systems. Apparently, Sir Francis Galton once remarked that 'until the data of any branch of human enquiry have been submitted to measurement, it cannot be said to have acquired the dignity of a science'. Three of the articles in the current volume make it clear that physical chemistry is quite capable of yielding fresh insights into complex biological phenomena. The first by Berne, Weeks and Zhou provides an excellent discussion of the fundamental issue of hydrophobicity and its differing nature on large and small



The collagen triple-helix polymer (top) and a single *N*-methylacetamine monomer (NMA) (bottom). The hyperpolarizability is shown as a hyperellipsoid. The net hyperpolarizability of collagen is equal to the coherent sum of the molecular tensors of its monomers in the weak coupling limit.

length scales. Theoretical challenges and controversies, as well as models ranging from the semiempirical Lum–Chandler–Weeks theory to the microscopic local molecular field theory are discussed. Amazingly, this is the only article in the entire volume that does not have even a single figure! Knobler and Gelbart educate us about the mechanisms by which a double stranded viral DNA is packaged into the capsid and later ejected into the host cell. The single molecule laser trap experiment summarized in figure 3 is highly informative and gives the reader an idea of how wonderful this ‘mean machine’ of nature is – packaging to crystalline densities, tens of piconewton force inside the capsid, and nearly 50 atmospheres of pressure exerted on the capsid walls. The success of simple analytical theories, outstanding challenges in terms of accurate estimates of the packaging rates and the dependence of the packing topology on capsid container shapes are clearly presented. In another well-written review, Fletcher and Geissler provide convincing arguments as to how active biological materials, making up a cell for instance, are very different from conventional materials. The authors have done a good job of motivating the theoretical challenges that need to be tackled in such systems exhibiting a complex interplay among various length, time and mass scales. So, for example, can one think of muscle fibres as usual materials with elastic modulus and viscous creep or we need to worry about the cytoskeletal activity involving filaments, motors, proteins, etc.? Using the example of growing actin filaments clearly brings out the central message – conventional approximations, in terms of properties and response, which are valid for static ordinary materials are rather poor when it comes to active biological materials. It seems like nature can integrate material responses with molecular controls with the utmost craftsmanship.

Finally, the article on equation-free multiscale computation by Kevrekidis and Samaey discusses a technique that should be useful in theoretical studies of many of the systems mentioned here. For complex systems one would like to simulate the microscopic dynamics on a long enough time scale to capture the emergence of novel and interesting phenomena on the macroscopic scale. However, despite knowing the microscopic evolution laws, the task is computationally dif-

ficult if not impossible. How does one come up with coarse-grained evolution equations with experimentally relevant approximations? Such a methodology is described in an exceptionally clear way by the authors. Three examples, although a bit sketchy on the details, provide a glimpse into the advantages of the approach and the difficult issues that still need to be resolved are mentioned. Interestingly, a very recent work by Noé *et al.* (*PNAS*, November 2009, early edition) adopts a similar philosophy in characterizing the equilibrium ensemble of protein folding pathways using short off-equilibrium simulations. Computer simulations of DNA packaging described by Knobler and Gelbart, for instance, would require some such approach in the near future.

I hope that the glimpse of the exciting advances in physical chemistry mentioned above is motivation enough to go and look up the current *ARPC*. For libraries it is a must and for those of you lucky enough to have a personal copy – happy reading!

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Economics of Forest Resources. Gregory S. Amacher, Markku Ollikainen and Erkki A. Koskela. The MIT Press, 55 Hayward Street, Cambridge, MA-02142. 2009. xxiv + 397 pp. Price: \$60.00.

The history of forest economics tracks the history of forestry. Just like the science of forestry began as the science of timber management, so did forest eco-

nomics begin as the economics of timber. The economics of timber deals with a straightforward question facing the owner of a piece of forest land. At what age should he cut the trees in a forest? This question can be broken down into a series of simpler questions, asked again and again. Should he cut the trees now, or wait a year before cutting them? If he cuts them now, then he gets the cash in his bank account right away, which can be invested at some interest rate, say r . If he waits a year, then the trees will have grown in the meantime, so he will get a larger sum of money, but will have foregone the interest he could have earned in the meantime from the proceeds of the sale of the timber. In 1849, a German forester, Martin Faustmann, was the first to publish a solution to the problem that took account of a second factor: cutting the trees now rather than delaying brings forward the profits from all future planting and felling cycles, and thus reduces foregone interest from those cycles. This solution to the problem became known as the Faustmann rule. The trees should be cut at the age when the gain from waiting a little longer is neither more nor less than the loss of interest from waiting a little longer. The gain from waiting a little longer is the value of the additional timber that accrues over the period of waiting. This, of course, depends on the price of timber and the rate of growth of the trees. The cost of waiting is the interest foregone over that period from not having sold the timber and invested the proceeds, as well as the interest losses from having delayed all future harvesting cycles.

It was soon realized that Faustmann's solution was correct. It is instructive to compare it with a solution popular among government foresters, that of choosing the rotation age to maximize the average yield of timber per year, also known as the mean annual increment. The problem with this solution is that it ignores the interest cost of delay.

Timber and pulpwood remained the primary interest for forest managers the world over until the last few decades of the twentieth century when other concerns assumed importance. (It is true that agrarian and tribal communities who managed forests had always had other interests, but these managers were not reading and funding forestry science. Managers acting on behalf of governments and corporations were.) Following the interest in recreational and amenity