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Preface

This special thematic issue of chemical physics 'Energy and entropy of change: From elementary processes to biology' celebrates the 80th birthday of Prof. Raphael D. Levine, known as Raphy

As suggested by the title of this special issue, Raphy's work spanned a diverse range of topics and complexity emphasizing concepts and a vision. At the beginning of his carrier, Raphy was one of the pioneers of what was considered the emerging new field of reaction dynamics. His book, 'Quantum Mechanics of Molecular Rate Processes' [1] published in 1969 was the state-of-the-art and strongly contributed to our early understanding of the field. His seminal book with Dick Bernstein 'Molecular Reaction Dynamics' (1974, [2] revised version 1987 [3], new edition 2005 [4]) served to establish the new field. It melded experiment and theory providing accessible and intuitive connections. At the same time, Raphy developed Surprisal Analysis, an information theoretic approach grounded in thermodynamics, that first was applied to analyze reaction dynamics data and identified the dynamical constraints that control energy and entropy changes. Then using algebraic techniques, Raphy and his collaborators showed that surprisal analysis is a predictive tool for energy and chemical changes during a reaction. Surprisal analysis became a term recognized by IUPAC and is nowadays used extensively across multiple fields, from nuclear physics to biology (see papers in this issue), and in engineering and in economics. The recent applications of Surprisal Analysis to big omic data (genomic, proteomic and metabolic) provides a foundation for the development of quantitative personalized medicine. Other recent fields of controlled molecular dynamics where Raphy is very active are in attochemistry and dynamics on several electronic states and in molecular logic.

Raphy's pioneering role in reaction dynamics is also reflected in his key role together with Prof. Ludwig Hofacker, Professor of theoretical chemistry at the Technical University of Munich, in founding this journal, Chemical Physics which first appeared in 1973. The idea emerged from their discussions during a visit of Ludwig Hofacker in Jerusalem. It was later finalized at a meeting in the Bavarian Alps with Dr Wimmers of North Holland and Ludwig Hofacker. With Richard Zare Raphy started Molecular Dynamics News in 1974 which remains to this day a major communication medium for physical chemists. With the support of Dick Bernstein and Dudley Herschbach, Raphy convened in Jerusalem in 1986 a workshop that was to become the first biannual stereodynamics meeting.

A recent autobiography of Raphy can be found in Annual Reviews of Physical Chemistry [5]. Raphy is the recipient of several scientific distinctions and prizes, among which are the Israel Prize in exact sciences (1974), the Wolf Prize (1988, with Joshua Jortner), the Rothschild Prize (1992), the Max Planck Prize for International collaboration (1996) and the EMET Prize (2002). He is a member of the Israel Academy of Sciences and Humanities, the Max Planck Society, Academia Europaea, American Academy of Arts & Sciences, American Philosophical Society, Royal Danish Academy of Sciences and Letters, and National Academy of Sciences of the United States. He has collected a number of medals starting in 1968 with the medal of the International Academy of Quantum Molecular Science and most recently in 2012 with the gold medal of the Israel Chemical Society. He is the (co)author of more than 700 papers. Raphy also mentored an outstanding number of PhD students and postdocs. They are holding academic positions in every research institution in Israel and in leading universities and research centers in the United States, in Europe and in Japan. Several of former Raphy's students are also successful entrepreneurs in the high tech industry in Israel. Currently Raphy is the Max Born Emeritus Professor of Natural Philosophy at the Hebrew University and a Distinguished Professor at the University of California, Los Angeles. In both he continues to engage in cutting edge science and in mentoring students.

The contributions to this special issue span the entire rainbow of research about energy and entropy change that Raphy has pioneered and shaped.

Two articles discuss recent aspects of inelastic collision theory. Perreault et al. (150–153) report on cold (few Kelvin) inelastic collisions that occur in a single molecule beam of mixture of gases (here H_2 and HD and HD and D_2). Since the two colliding species are co-expanded in the same molecular beam, the magnitude of the relative velocity is rather low while the direction of the relative velocity is well defined which allows studying stereodynamics effects in rotational inelastic collisions. Such a technique allows for the observation of orbiting resonances. An extension of the quasi quantum treatment for rotational inelastic NO(X)-He collisions to the mixed Hund's case (a) spin orbit state conserving and changing transitions is proposed by Zhang et al. (4–19). The new treatment compares well with exact quantum results and opens the way for the rotationally inelastic scattering at a thermal collision energy of molecules residing in a Π electronic rotational eigenstate. Collision dynamics between Rydberg molecules entrained in a supersonic molecular beam leads to the formation of an ultracold plasma on a nanosecond time scale. Haene et al. (55–66) show in their contribution that coupled rate equations simulations faithfully capture the kinetics of the avalanche dynamical process and the dissociation channels. The contribution of D. Ben-Amotz (113–119) also deals with collision theory in a broad sense and focuses on the similarities between thermally equilibrated photons and an ideal gas of highly relativistic ultralight particles requiring that the results of kinetic theory be consistent with independently obtained results of thermodynamics and electromagnetic theory.

A connection is established by Moro et al. (141–149) between the equilibration dynamics of a pure initial state initially localized at a given site of a 1D disordered chain and the amplitude of dynamical

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fluctuations of a typical random pure state. Different measures of Anderson localization are compared. In their contribution, Daskin et al. (87–94) propose a quantum circuit for implementing the phase estimation algorithm of the eigenvalues of a Hamiltonian. They show that for a certain class of Hamiltonians, the phase algorithm can be realized via successive applications, without matrix exponentiation. The quantum and classical complexities of the quantum circuit are analyzed for Hamiltonians that can be written as a sum of unitary matrices and the ground state energy of the H_2 computed as an illustrative example.

Ultrafast electronic dynamics and concerted electronic motion in molecules and nanodevices are discussed in the contributions of Diestler et al., (66–77) Yang et al. (120–125) and Lehman et al. (176–182) Diestler et al. (67–77) compare approximate and exact results for concerted electronic and nuclear fluxes associated with electronically adiabatic processes on the ground state of aligned vibrating $H_2^+(^2\Sigma_g^+)$, a system for which wave function can be obtained. The validity of the Born Oppenheimer approximation and the role of electron correlation are discussed in connection with Born-Huang expansion and exact results. In Yang et al., (120–125) the stepwise or concerted nature of the reaction mechanism for the dimerization of cyclopentadiene on the ground electronic state is analyzed in the framework of the Born-Oppenheimer approximation, using transition state theory and direct molecular dynamics (MD) trajectories. Transition states obtained at the DFT level with various functionals have an ambimodal character. This ambimodal character is consistent with the results of classical MD. 70% of the trajectories correspond to a concerted mechanism, while 30% are dynamically stepwise. In those 30%, 13% follow a two-stage mechanism that involves the Cope transition state. The characteristics of electronic transport and current are also essential in nanoelectronics. Lehman et al. (176–182) investigate the dynamics of electron transport and currents using a non equilbrium Green's function formalism based on an extension of the auxilary mode formalism in the wide band limit. Using this modeling approach, they analyze the role of the contact contribution to the current as well the role of interferences in benzene rings with contacted in meta or para positions.

Electronic dynamics in the excited states of the photoexcited CO molecule strongly affects the carbon and oxygen fractionations during its dissociation. Chakraborty et al. (78–86) report on their measurements of the photodissociation crossections of isotopologues of CO at 80 K using VUV light. Perturbation dominated state mixing determines which isotopologues preferentially dissociate. The predissociation can be direct or indirect. There is a strong temperature dependence on the isotope effect. A valuable spectroscopic approach to disentangle vibrational coherence in multi electronic state dynamics is to combine 2D electronic with resonant and non-resonant Raman spectroscopies. In their contribution, Meneghin et al. (132–140) apply this novel approach to investigate the ground and excited electronic state vibration in Chlorophyll *a* excited with short fs laser pulses. They show that the combined approach allows the clear identification of the vibrational modes that are strongly involved in the electronic coherence.

Molecular dynamics simulations are a valuable tool for computing vibrational spectra of anharmonic molecular systems. In their contribution, Sagiv et al. (44–54) apply the *ab initio* classical separable potential (AICSP) methodology for computing anharmonic frequencies of carbonic acid, its dimer and complex with H_2O as well as some isotopologues. This newly developed method is based on building separable potentials for each normal coordinate from averaging over classical trajectories and solving the time-dependent Schroedinger equation. AICSP is shown to give OH and CO frequencies in better agreement with experimental results than the harmonic approximation. Anharmonicity and Fermi resonances play a crucial role in the understanding proton transfer in water. Samala et al. (164–175) report on a detailed computational study of the infrared spectrum of the protonated water trimer, a prototype of a proton wire that can transport two protons in a concerted fashion. They compare infra-red spectra computed with two different approaches: vibrational second order perturbation theory and *ab initio* MD trajectories. The implications for proton transfer in water of a giant Fermi resonance between the proton transfer mode and two combination modes in the non deuterated species is discussed.

For larger systems like biopolymers, membranes and proteins, one typically resorts to coarse-grained molecular dynamics where approximate potentials describe the interactions between the monomeric units. Allolio et al. (31–43) propose a new methodology, the real space instantaneous local method, for extracting bending and tilt moduli of membranes from coarse-grained molecular dynamics simulations. This methodology is designed for highly dynamics systems with arbitrary interfaces. A detailed comparison is provided with other existing approaches. Coarse grained MD simulations are used by Bigman et al. (95–105) to investigate how tethering a conjugate on a protein influences its thermodynamic stability, that is the relative stability of the unfolded and folded forms. The conjugate is found to affect the unfolded state by eliminating residual interactions which leads to an increase in its configurational entropy that is not compensated by the enthalpy change, resulting in a lower free energy for the conjugate than of the wild type. This stabilization of the unfolded form leads a thermodynamical destabilization of the protein.

Photoinduced fragmentation and photoionization are becoming important tools for analytic purposes. Neidel et al. (106–112) report on femto second laser induced dissociation combined with mass spectrometry analysis of the fragmentation patterns as a promising tool for peptide sequencing. This approach is particularly valuable for peptides exhibiting post-translational modifications. In their contribution, Kruve et al. (126–131) describe how a novel analytical technique based on electron multiphoton extraction spectroscopy provides a quantitative and sensitive mapping of imidacloprid (present in pesticids) in plants. Imaging and quantitative analyses are demonstrated on several plant surfaces including olive and mint leaves and orange peel. The performances of this new analytical technique are discussed.

In recent years, Raphy and his collaborators have applied surprisal analysis to very different types of biological omic data (mRNA, miRNA, proteins, metabolites) of different organisms (yeast, unicellular algae, cell lines, patients data). In this issue, Willamme et al. (154–163) report on the surprisal analysis of mRNAseq data of a mutant and a complemented (control) strain of the green unicellular micro alga *Chlamydomonas reinhardtii* subject to day/night cycle growth conditions in the presence of acetate. Constraints and gene pathways that discriminate between mutant and control samples are identified. Carbon metabolism dominates in the light phase for the control strain while the dark phase is enriched in cell division pathways. The mutant phenotype includes genes pathways of stress response and autophagy in the two phases. Flashner-Abramson et al. (20–30) use surprisal analysis to investigate the protein response of a human mammary cell line exposed to the epidermal growth factor (EGF) to a treatment with the SRC family kinase inhibitor dasatinib. Surprisal analysis resolves the unbalanced protein networks that result from the exposure to EGF and allows predicting the response to the drug.

Raphy, over the pass 60 years or so, you were a great and inspiring scientist, teacher, collaborator, colleague, and a friend. We wish you a very happy 80th birthday and many more fruitful and stimulating scientific adventures in the years to come.

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