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SPECIAL ISSUE PREFACE

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Tribute to Shaul Mukamel

With great pleasure, we honor Shaul Mukamel on his 60th birthday and recognize his contributions to both physical chemistry and chemical physics. Shaul's most significant contributions are directly related to nonlinear time-domain spectroscopy of condensed phases. Modern spectroscopy, being a tool of extremely high precision, still provides detailed information on the underlying photoinduced dynamics and relaxation processes in a rather indirect way. The situation is even more complicated due to the existence of a broad variety of nonlinear spectroscopic techniques, as well as the intrinsic complexity of the underlying dynamical phenomena, including typically strong electron correlations, the delocalized nature of electronic excitations in molecular systems, strong coupling to vibrational modes, and the macroscopic number of bath degrees of freedom. Over the years, Shaul has developed and systemized theoretical approaches and computational methods to establish stable links between dynamical phenomena and spectroscopic signals. This continuous effort led to the creation of a new field that may be referred to as *Theoretical Spectroscopy*. The aim of this endeavor is to discover and implement practical methods that relate nonlinear spectroscopic signals in condensed phases to specific dynamical features, so that dynamical information may be retrieved from experimental data in the most straightforward, clear, and unambiguous way.

This goal could not have been reached without developing a number of new key concepts and implementing nontraditional approaches. On the fundamental side, Shaul customized Liouville space quantum dynamics, adapting it to become the main tool of theoretical spectroscopy. Second, he established a quasiparticle (weakly anharmonic oscillator) view of optical response in many-particle systems, and third, he imported into the subject the many-body approaches of condensed matter and field theory that were not traditional to the physical chemistry community. On the applications side, by formulating spectroscopy on different time and frequency scales within a unified framework, Shaul established strong analogies between apparently different dynamical phenomena or different spectroscopic techniques, which in turn fostered a useful transmission of ideas between different fields. In particular, in the mid 1990s, by using an analogy between multiphoton optical processes and multiquantum NMR, Shaul developed a series of spectroscopic techniques, now collectively known as *2D-spectroscopy*, that currently are used abundantly as ideal probes of electronic and vibrational dynamics in many materials and biosystems.

Liouville space quantum dynamics has become an absolutely necessary tool in modern spectroscopy. As opposed to its linear counterpart, nonlinear response is intrinsically nonequilibrium in nature, and the existing approaches, based on analytical continuations of the Matsubara (imaginary-time) Green functions, do not appear to be feasible. The nonequilibrium techniques, based on the Keldysh double-time loop, have become a traditional tool in condensed-matter theory. However, the latter, while being very efficient in the frequency domain, does not keep track of time ordering.

The Liouville space approach, developed by Shaul, although formally equivalent to the Keldysh loop, has the advantage of keeping the order in real time. As a result, Shaul developed a general interpretation of nonlinear response in terms of double sided Liouville space diagrams, which became *the* standard for interpretation of experimental nonlinear spectroscopic data. It is not surprising that Shaul's book *Principles of Nonlinear Optical Spectroscopy* became a standard textbook for graduate students studying physical chemistry, as well as a complete reference monograph for all experimentalists and theorists dealing with techniques of nonlinear optical spectroscopy.

In traditional quantum chemistry, molecules are characterized by their electronic eigenstates, and their linear and nonlinear response functions are represented using the famous Bloembergen sum-over-states expressions. However, in large molecules, the electronic spectra become so dense that the molecular optical properties are related to the statistical properties of the energy levels (adequately described in terms of the many-body Green function techniques), rather than their exact positions. By formulating equations of motion for a set of reduced many-body

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variables, Shaul introduced a quasiparticle picture of optical response, where the basic object is linearly coupled to the optical field harmonic oscillator, rather than a two-level system; the optical nonlinearities occur due to weak anharmonic coupling among the oscillators, and consequently nonlinear optical response can be viewed as arising from quasiparticle scattering.

The quasiparticle approach, developed by Shaul, led to clear and transparent interpretations of the optical properties of large conjugated molecules and superstructures, photoinduced dynamics of Frenkel-exciton systems, including J-aggregates, superlattices, and photosynthetic light-harvesting complexes, optical properties of semiconductor quantum dots and quantum wells, and spectroscopy of vibrational excitons in biological molecules. Notably, the quasiparticle approach has solved a major problem of size-consistency in the sum-over-states expression by obtaining the correct $\sim N$ scaling of the third-order susceptibilities directly, completely bypassing numerical cancellation of the much larger $\sim N^2$ terms.

Shaul's wide knowledge of physics, chemistry, and mathematics, in combination with his boundless creativity, imagination, and energy, allows him to keep pushing the limits. As a result, it is impossible to imagine him fitting within any kind of conventional framework, so that femtosecond time scales are not enough for him. Over the past decade, while still focusing on femtosecond spectroscopy, Shaul moved to different time scales, notably, in both directions: much faster attosecond spectroscopy in the X-ray spectral region and much slower single-molecule spectroscopy. His research on single-molecule dynamics is, of cause, centered on the most complex issues of quantum effects, where measurement-induced wave function collapse plays a crucial role. Shaul has pioneered some truly nontrivial quantum generalizations of nonequilibrium fluctuation and work relations. If one were to ask what Shaul's scientific interests actually are, everything connected with dynamics would probably be the most adequate answer. Correlation spectroscopy with entangled photons, the fundamental issues of entanglement, nonlinear single-molecule spectroscopy, and the interplay of chaos and quantum effects in nonlinear response would be a very incomplete list of the "toys" Shaul is currently playing with.

In 2003, Shaul moved from rainy and snowy Rochester to sunny Irvine. Despite this change of venue, his lifestyle is basically the same. He is always active, always positive, always humorous, and always focused on science—despite having multiple responsibilities. Shaul is forever thinking of new experiments, forever thinking of new formalisms, and forever interested in fundamental questions. If you are a student or a postdoc and you are complaining that it is difficult for you to reach your advisor, join Shaul's research group. If you wish to distract Shaul from doing something important, tell him something like this: "Shaul, I found a missing term in the field-polarization interaction Hamiltonian." If you want to ruin a quiet Saturday evening at the Mukamel residence, call him and tell him you are at work and just found something interesting. Happy Birthday, Shaul!

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