

Autobiography of Shaul Mukamel

I was born in Baghdad, Iraq, on December 11, 1948. Mesopotamia, now Iraq, had an old Jewish community that dated back 2600 years from the time of the destruction of the first Jewish Temple in Jerusalem. The Jews of Mesopotamia excelled as merchants, craftsmen, and rabbinic scholars. They created the Talmud, an important analysis of the Jewish legal code. The vast majority of the Jews immigrated to the state of Israel when it was created, leaving behind their long history, their property, and their ancestors. One of mine, Rabbi Isaac Salem Mukamel, had written a few books. "Netivot Issac", printed in Jerusalem in 1923 and circulated in Baghdad, predicts the lunar calendar and eclipses for many years into the future. The lunar calendar is used by Jewish religious scholars, to identify the time for yearly holidays and daily prayers. My family immigrated to Israel in 1951, and I grew up in Tel Aviv. Israel's economy was weak in the early 1950s. The country was absorbing new immigrants, and the infrastructure had yet to be developed. My parents, Meir and Marcel, made acquiring the very best possible education for me and my two older brothers and sister their highest priority despite considerable financial difficulties in making a living from a grocery store. High school tuition was prohibitively high, and getting all of us through school was a major challenge.

Municipal School A, my high school in Tel Aviv, was unique. The teachers were mostly passionate new immigrants with extremely high qualifications, many of whom held Ph.D.'s. The school had very high standards, placed a strong emphasis on science, and offered numerous opportunities for extracurricular activities. Former graduates of the school from my generation have gone on to assume top positions in academia, business, government, medicine, politics, and journalism. (Joshua Jortner and Raoul Kopelman were classmates in the same school some years earlier.) Science was highly valued in Israeli society. The first President (Dr. Chaim Weitzman) was a chemist, and Albert Einstein was offered the presidency (which he declined). Scientists were respected and played important roles in the formation of the new state of Israel.

I began undergraduate studies after graduating from high school in 1966 at the newly created department of chemistry of Tel Aviv University. The department was led by Joshua Jortner who came from the Chicago School of Chemical Physics and attracted many young highly motivated and energetic faculty. I graduated in 1969 and then did my master thesis with Uzi Kaldor, working on electronic structure calculations of the excited states and electronic spectroscopy of He_2 . Computer codes in those days were written on decks of punch cards. Afterwards, I joined the group of Joshua Jortner to work on my Ph.D. The group was vibrant and very large by Israeli (and international) standards with about 20 members. There was a constant flow of stimulating visitors from all over the world and at all levels. Joshua was a great advisor with a deep, broad grasp of chemistry and physics and a limitless, infectious, and optimistic enthusiasm. Since he held numerous administrative positions, including the vice presidency of the University, we worked mostly at night, often until the early morning hours, to the dismay of his wife, Ruth. I vividly remember Richard Bensohn from Columbia University who visited regularly and insisted on giving a graduate

class using his Biblical Hebrew. The students protested and requested that the class be given in English.

I started to work on the theory of radiationless transitions and the photophysics of organic molecules in the condensed phase, following the earlier pioneering work of Bixon and Jortner and Rudy Marcus's theory of electron transfer. Among my contemporary graduate students were Abe Nitzan with whom I collaborated on the study of vibrational relaxation (a highly cited work to date) and Yosi Klafter. Jortner used to work very closely with one of his star students who was the most productive at the time and paid very little attention to everyone else. I had to wait until Nitzan graduated in order to receive his full attention, and Klafter had to wait until I graduated. The department was truly international and offered an unusually stimulating environment. I also greatly appreciated the many opportunities I had to attend conferences, workshops, and schools in Europe, and even Brazil.

One experience that completely changed my perspective and opened my eyes to the most advanced contemporary research in optics and spectroscopy was a three month winter school held at the International Center for Theoretical Physics in Trieste in 1971 that was led by Alfred Kastler who had received the 1966 Nobel Prize for his optical pumping work (a combination of optical and magnetic resonance in atoms). The center's director, Mohammad Abdus Salam, was closely engaged in the school activities. Kastler had made a very careful choice of speakers. He attended all the lectures and made wonderful and insightful comments. Among the lecturers were Claude Cohen-Tannoudji, Jean Brossel, Gerhard Herzberg, and Serge Haroche. This school exposed me to the French School of Atomic Physics and Quantum Optics and completely changed my scientific career. I was impressed by Herzberg's encyclopedic memory and his deep understanding of molecular spectra. He showed many unmarked slides of spectra of different molecules in his lectures and analyzed them and their symmetries without any notes, simply by inspection. His only difficulty was to persuade the Italian projectionist to go back occasionally to the previous slide. He desperately repeated "primera fotografica", which I understood perfectly, but the projectionist did not. The Frontiers in Laser Spectroscopy Summer School in Les Houches in 1975 was also instrumental in shaping my future work. Many exciting topics such as superfluorescence were discussed. Among the speakers were Hermann Haken, Roy Glauber, and Leo Kadanoff.

I published several articles in *J. Chem. Phys.* during my graduate studies. I recall submitting one long manuscript including 30 figures which the referee politely recommended be considerably shortened. Jortner's reply was that we completely agreed with all the useful recommendations of the referee and were able to eliminate Figure 19C. The paper was accepted by the legendary editor Willard Stout, and that was a great lesson to me: Never argue with referees.

My interest at the time focused on the theory of molecular photodissociation. I developed Green's function time domain

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techniques which provided good insight into the dynamics of the process, and showed how to incorporate intramolecular vibrational dynamics in radiative and nonradiative processes in isolated molecules. The time-domain Green's function treatment of preparation and decay of excited states paved the way for the wave packet description of molecular spectroscopy and provided a microscopic basis for the future analysis of spectroscopy of ultracold molecules in supersonic beams and infrared multiphoton chemistry. Similar ideas were developed by Eric Heller during the same time. We speculated that fast femtosecond pulses could be used to detect wave packet evolution. Ultrafast lasers were in their infancy, and this seemed like a remote dream; we stated that it might never be realized. One of Jortner's students was unsuccessfully trying to duplicate Peter Rentzepis' experiments on the picosecond dynamics of internal conversion in azulene. Peter came from Bell Labs for a visit. He worked extremely hard and finally the laser started operating (perhaps with the help of an unspecified drink that Peter brought). Jortner held a reception for Peter, and one of the guests asked him what sightseeing he had arranged for his visit. Peter looked at him and immediately replied: "To tell you the truth, the only place I have seen in Israel during my visit was the basement of the chemistry department".

In 1975, toward the end of my graduate studies, the field of laser chemistry was launched by several reports of selective dissociation of SF_6 by intense CO_2 laser (frequency 1000 cm^{-1}). The dissociation, first reported by Abratzumian Ryabov with Letokov, was a 10-photon process. It generated great excitement and raised hope that laser selective chemistry might be used to direct and control reactions to different products than are possible thermally. One application that drew considerable scientific and government attention was the possibility of laser induced isotope separation, leading to many schemes to achieve this goal in atoms and in molecules. This was my first exposure to a rapidly developing field where international conferences were held on almost a weekly basis and results received extensive coverage in the regular press. I studied and calculated possible mechanisms of selective multiphoton dissociation and how it could compete with intramolecular vibrational redistribution (IVR) so that coherence could be maintained long enough for chemical processes to occur prior to energy thermalization.

I received my Ph.D. in 1976 and started my postdoctoral work at MIT in 1977, working with Irwin Oppenheim and John Ross on stochastic dynamics. The classic line shape theory of Kubo and a review article by Van Kampen on the cumulant expansion which had just appeared became extremely helpful in my future work on multidimensional spectroscopy. I vividly remember one anecdote in a seminar given by Nico Van Kampen, who was a frequent visitor at MIT. He talked about a certain parameter (I forgot what it was) which was found to be 0.7, whereas conventional theory predicted it to be 1. He then went ahead to argue that this was a huge and unacceptable discrepancy and outlined elaborate theoretical ways for bridging the gap. This type of concern was a culture shock to me. In Jortner's group, we were accustomed to working on "Big" issues and any calculation that lay within two orders of magnitude of experiment was considered a great agreement.

I had the wonderful opportunity in 1977 to collaborate with Nicholas Bloembergen, Eli Yablonovich, and their student Jerry Black at Harvard on the interpretation of their careful multiphoton dissociation study of SF_6 . Experiments and analysis showed this was a thermal process: due to anharmonicities and

the high density of vibrational states, IVR takes place before any bond can break, and the laser was just serving as an expensive heating device. This and other studies caused the wide interest in laser chemistry to sharply decline. Selectivity and coherence effects were not possible by simply subjecting a molecule to an intense noisy infrared laser. The field was revived several years later with the development of femtosecond sources with stable phases, and coherent control schemes which allowed for the rational design and realization of laser selective chemistry.

Abraham Ben Reuven joined the faculty in Tel Aviv, from the Weizmann Institute, toward the end of my Ph.D. There was a debate at the time about how to distinguish between resonant Raman and fluorescence, triggered by experiments in I_2 by Williams, Rousseau, and Dworetzky. Robin Hochstrasser was working independently on the problem. This subtle distinction is still confusing and is repeatedly being rediscovered and revisited in the current literature. Abraham was an expert in the Liouville space density matrix approach to spectroscopy working with Ugo Fano who had developed this approach for pressure broadening of spectral lines. Similar work was done by Phil Anderson during his Ph.D. Bob Zwanzig, Sadao Nakajima, and Hazime Mori had developed projection operator techniques in Liouville space for dissipative dynamics. It became clear to us that all the pieces fall nicely into place by formulating the problem using the density matrix in Liouville space. It is impossible to understand what is going on when working with wave functions in Hilbert space. As we tune the excitation frequency, spontaneous light scattering gradually changes from resonant fluorescence to off resonant Raman. Conventionally, we say that a "real" transition becomes "virtual", but there is no clear qualitative distinction between the two in Hilbert space, since the variation is smooth and continuous, this issue remains a mystery. In Liouville space, in contrast, the process naturally separates into distinct pathways and one can clearly identify Raman and fluorescence paths. This work had a profound influence on my future career. I am deeply indebted to Ben Reuven for introducing me to this powerful technique and language. In retrospect, my entire career has been a series of adventures in Liouville space. I calculated the pressure and detuning behavior of the iodine experiments. While Jortner was on sabbatical at Caltech, he sent me a complete clearly written draft of a manuscript before even seeing the results of the calculations. The last section said that the agreement of theory with experiment was poor/good/excellent. All I had to do was check mark the right box and submit the paper.

A few years later in 1989, while I was working with Yuming Hu on the theory of sequential vs tunneling (superexchange) electron transfer, we realized that this problem is formally identical to the fluorescence/Raman issue. Liouville space pathways are thus extremely helpful for analyzing long-range electron and energy transfer in proteins, chromophore aggregates, and biological complexes. The primary events in the photosynthetic reaction center and the related antennae are controlled by long-range spatial coherence (i.e., phase information among well-separated chromophores). The fundamental relationship between sequential and direct (superexchange) contributions to long-range electron transfer and fluorescence and Raman spectroscopy may be established by formulating both phenomena in terms of the density matrix.

I had the opportunity to meet Fano in Chicago. He was kind enough to offer very crisp comments on a draft of the Liouville space chapter in my book, and he told me about the history of his famous paper on the Fano Lineshape in the photoionization of

atoms. The topic was suggested to him by his Ph.D. advisor, Enrico Fermi. Fano struggled for two years to get it right. He later accidentally discovered that Fermi had it all worked out in his notes, before he gave him the problem.

I received a Weizmann Fellowship and moved to UC Berkeley where intensive work was being done on laser chemistry by Yuan Lee, Ron Shen, and Brad Moore. I interacted closely with Charles Harris and Alex Pines, and I became interested in multiquantum NMR, which connected well with my previous experience at Kastler's school and with multiphoton dissociation. The degree of pulse control in radio waves was unimaginable for optical frequencies at the time. The analogy between multiphoton optical processes and multiquantum NMR was intriguing and raised my interest in transferring NMR techniques and methodologies to the optical regime. Working with a young and ambitious first year graduate student of Pines, Warren Warren, we prepared a draft of an article comparing the two. That article is still buried somewhere on Alex Pines' desk and never saw the light of day. Warren was irritated about that for a decade. Thirty years later, we both lost hope for it to ever be published.

In 1978, I moved to Rice University where I collaborated with Rick Smalley, who had just set up his supersonic beam apparatus to obtain frequency domain fluorescence measurements of cold molecules at cryogenic temperatures (nothing like the present ultracold nanokelvin technology) allowing much better resolution compared to room temperature spectra. His students were focusing on finding the triplet state energies of small radical, before I convinced them that IVR was an important issue and suggested they study it in various alkyl-substituted benzenes. Although the data showed some indirect evidence, it was clear that only time-domain measurements could provide clear-cut and unambiguous probes for IVR. When I discussed this with Rick, he said, "Only Zewail can do it!" These experiments were indeed performed a few years later by Zewail.

I returned to the U.S. in 1982 after a brief stay at the Weizmann Institute as an associate professor at the University of Rochester. When I arrived in Rochester, I thought it would help me getting funded if I were to organize a conference on IVR. Several agencies had turned me down, but the AFOSR was very generous and eager to cover the cost even beyond what I had requested (this has never happened to me since!). Four of its grant officers attended. I invited about 30 speakers to Rochester; the meeting went very well and reflected the excitement surrounding the topic. Ahmed Zewail, who was doing picosecond measurements in molecular beams at the time, gave a very impressive talk, forcefully laying out the argument for carrying out femtosecond experiments that could directly and unambiguously monitor vibrational motions. The outcome of the meeting was that he received a commitment on the spot for substantial AFOSR funding to build his first femtosecond system. No funding was left for my ambitious theoretical effort. My meeting was too successful! In retrospect, I take some comfort that this was my modest contribution to starting the field of femtochemistry. Femtosecond lasers in the early 1980s opened up the way to probe photophysical processes of chemical reactions in real time. I worked on extending the Liouville space pathway approach to nonlinear spectroscopy, recognizing how the field of ultrafast molecular nonlinear spectroscopy badly needed a unified approach that could describe and compare the various signals. Numerous confusing terminologies and four letter acronyms were commonly used to describe the same measurements, and it was not possible at the time to systematically and

rationally design an experiment for probing specific processes. I gave a graduate class at Rochester which did precisely that. It took me over 10 years to complete my book "Principles of Nonlinear Optical Spectroscopy" which finally appeared in 1995 and had helped create a common language that is widely used for the interpretation of signals and the design of new measurements. The group of Douwe Wiersma made first use of this formalism to analyze their femtosecond condensed phase measurements. I provided them with a draft of my book, and his students made good use of it. These were first reported in the excellent thesis of Eric Nijbering. At Rochester, I enjoyed in-depth lunch discussions with two leading giants in classical and quantum optics: Len Mandel and Emil Wolf.

My first paper with Yijing Yan and Larry Fried, on applying the Liouville space formalism to the ICN photodissociation experiments of Zewail, was submitted to *J. Chem. Phys.* The referees were very skeptical; one referee said something like "Mukamel has a high reputation, and to save this reputation, he should not publish this useless article." The paper was finally published in *J. Phys. Chem.* in 1989. *J. Phys. Chem.* at the time was assuming a leadership role in chemical physics, thanks to the heroic efforts of its editor, Mostafa El Sayed, who was bombarding the community with solicitations of novel articles. Yijing Yan had then obtained a postdoctoral position with Kent Wilson. Kent was a true visionary and had many pioneering ideas regarding the simulation and multimedia visualization of chemical dynamics that were far ahead of his time. He was one of the very first to recognize the enormous possibilities offered by phase-controlled optical pulses and had launched a unique and ambitious self-funded experimental and theoretical effort to develop these ideas. Undergraduate and computer science students were widely integrated in his research and education program. In a collaborative effort in 1993, we had formulated the coherent control ideas of Stuart Rice, David Tannor, Hersch Rabitz, Paul Brumer, and Moshe Shapiro using the density matrix in Liouville space and using the perturbative response function approach. This provided new tools for the computation and analysis of coherent control schemes which up to that point had all focused on the wave function in Hilbert space, and allowed the treatment of dissipative dynamics in open systems. With Ian Walmsley, we demonstrated in 1995 an application of the Liouville space approach to wave function tomography.

After attending the 1996 Nobel Symposium on Femtochemistry and Femtobiology, I spent the last night in Stockholm together with Graham Fleming, Chuck Shank, and Robin Hochstrasser. We decided to go to dinner, and Robin, with his unwavering and unshaken confidence, recommended a good restaurant and even volunteered to guide us using a map that he proudly pulled out of his pocket. After walking 20 min in heavy rain through the streets of Stockholm with no restaurant in sight, Robin suddenly uttered "Oh my God, this is a map of Vienna...."

Multidimensional optical spectroscopy was developed by close examination and attempts to unify the description of various experiments. Linear absorption provides a one-dimensional (1D) projection of molecular information onto a single frequency axis through the linear polarization induced in the sample to first order in the field. Higher-order polarizations, and more complex molecular events, can be revealed by nonlinear spectroscopic techniques. Techniques such as fluorescence, spontaneous Raman, and pump probe are incoherent and independent of the phases of the laser pulses. Nonlinear spectra are modeled more simply when the relaxation rates of frequency

fluctuations Λ are either very fast or very slow compared to their magnitude Δ . This is well-known from the early work of Kubo. The famous paper of Bloembergen, Purcel, and Pound (1948) discusses motional narrowing in NMR. When such a time scale separation exists, these fluctuations can be treated phenomenologically as homogeneous ($\Lambda \gg \Delta$) or inhomogeneous ($\Lambda \ll \Delta$) line broadening. Picosecond, electronically off resonant, Coherent Anti-Stokes Raman Spectroscopy (CARS) measurements of vibrational dephasing in molecular liquids pioneered by Kaiser and Laubereau in the 1970s were believed to have the capacity to distinguish between the two broadening mechanisms. This capacity is well-known for the photon echo technique from the pioneering NMR work of Irwin Hahn whose visionary 1951 paper is truly amazing. Coherent resonant photon echoes in molecules had long been carried out by Mike Fayer and Douwe Wiersma. Warren Warren and Ahmed Zewail had investigated in 1998 the role of optical pulse phase control in nonlinear measurements. One of the problems obscuring the issue that led to this false belief was the semiclassical macroscopic analysis (quantum matter coupled to classical light) which requires the numerical propagation of Maxwell's equations in order to compute the signals. Working with Roger Loring in 1985, we had formulated the problem microscopically in terms of multi-point correlation functions of the electronic polarizability. The key lesson was that optical signals should be classified by their *dimensionality*, i.e., the number of externally controlled time intervals, rather than merely by the nonlinear order in the field. Both photon echo and electronically off resonant time-resolved CARS signals are four-wave mixing processes which are third order in the external fields. The off resonant CARS signal, however, has only one control time variable t_2 . The other two times t_1 and t_3 are very short, as dictated by the time-frequency Fourier uncertainty relation, and carry no molecular information. From this perspective, the technique is one-dimensional (1D), carries identical information to spontaneous Raman, and cannot *in principle* distinguish between the homogeneous and inhomogeneous mechanisms. We concluded, based on this analysis, that a two-dimensional Raman analogue of the photon echo would require seven rather than three pulses. Such experiments were subsequently carried out by Van Voorst and independently by Mark Berg. Closed expressions using the cumulant expansion for the multipoint correlation functions of a multilevel system whose frequencies undergo stochastic Gaussian fluctuations were derived in a *J. Opt. Soc. Am. B* article with Loring, paving the way for multidimensional simulations of such spectra. The multimode Brownian oscillator model for the nonlinear response, developed by Yijing Yan in a series of articles starting in 1984, generalized the stochastic approach to include finite temperature effects and the fluorescence Stokes shift. Massimiliano Sparapaglione developed similar ideas for solvation dynamics in adiabatic electron transfer. It has since been widely applied to describe the spectroscopic signatures of intramolecular, intermolecular, and solvent nuclear motions in liquids, glasses, polymers, and semiconductor quantum dots. In 1991, Graham Fleming's group reported fluorescence measurements with phase-locked pulses. During an Ultrafast Phenomena meeting, I pointed out to him that this can be viewed as a coherent nonlinear technique, and is naturally connected to other types of optical signals using the response function approach. No new formalism is required and numerous insights can be gained. Min Cho, a graduate student of Fleming, came to Rochester to explore this. He was able to master the Liouville space formalism in no time, and was instrumental in

applying it to ongoing experiments in Chicago, first to phase locked fluorescence and then to a broad range of other measurements.

As a concession to experimentalists, we subsequently proposed in 1993 a "simpler", five-pulse, impulsive off resonant Raman technique and showed how it can be interpreted using 2D frequency/frequency correlation plots. This work, with Yoshitaka Tanimura, pointed out the analogy with multidimensional NMR, and triggered intense experimental and theoretical activity. Experiments performed on low frequency ($<300\text{ cm}^{-1}$) intermolecular vibrations in liquid CS_2 were initially complicated by cascading effects (sequences of lower order processes). These were eventually resolved by the groups of Graham Fleming and Dwayne Miller. Working with Wei Min Zhang and Vladimir Chernyak in 1998 and 1999, we had extended the multidimensional techniques to resonant vibrational spectroscopy in the infrared and to electronic spectroscopy of excitons in the visible. Semiclassical simulation techniques were developed by Vladimir Chernyak and Andrei Piryatinski. Applications to semiconductor nanostructures were made by Torsen Meier, Martin Axt, and Satoshi Yokojima. Resonant techniques require fewer pulses, since each transition involves a single field, rather than two for a Raman process. The necessary control over the phase of some or all laser pulses, which is straightforward for radio waves (NMR), is considerably more challenging at higher frequencies. Coherent multidimensional spectroscopy in the infrared and the visible regimes has been developed rapidly over the past 18 years. A broad variety of infrared 2D techniques were demonstrated experimentally by Robin Hochstrasser, Mike Fayer, Thomas Elsaesser, Dwayne Miller, Peter Hamm, Marty Zanni, Andrei Tokmakoff, and others. In the visible, Graham Fleming, David Jonas, and Harald Kauffmann have applied the technique to molecular systems and Steve Cundiff has demonstrated its power for probing Wannier excitons in semiconductor quantum wells. These advances dramatically enhanced the temporal resolution from the millisecond to the femtosecond regime. These techniques can disentangle complex spectra and provide useful structural and dynamical information. The field of multidimensional spectroscopy is rapidly expanding. A biannual conference series devoted to this field is ongoing; the fifth conference was held in 2010 in Minnesota.

The 1993 article proposed a new class of coherent measurements employing sequences of multiple femtosecond pulses in order to gain structural and dynamical information unavailable from linear techniques. By extending ideas from NMR to the optical regime, we showed how analogous but different information can be extracted by combining heterodyne detected phase-controlled weak field signals generated at different phase matching directions. The 1D absorption spectrum provides information about excitation energies and transition dipoles projected into a single frequency axis. Multidimensional optical spectroscopy uses sequences of laser pulses to perturb or label the electronic and vibrational degrees of freedom and watch for correlated events taking place during several controlled time intervals. The resulting correlation plots can be interpreted in terms of multi-point correlation functions that carry considerably more detailed information on dynamical events than the two-point functions provided by any 1D technique. In 2001 and 2002, we explored the NMR analogies and their limitations in detail with Christoph Scheurer. Correlations between spins are routinely used in NMR to study complex molecules. Multidimensional optical techniques are similar to their NMR counterparts but with greatly improved temporal resolution. NMR experiments are performed

with strong pulses which move the entire spin population. Pulse sequences involving hundreds of pulses are then possible. In order to avoid photochemical processes, optical studies, in contrast, use weak pulses exciting only a small fraction of the molecules, limiting the applicability to only a few pulses. Each additional pulse results in a considerable reduction in the signal. The signals can then be calculated perturbatively, order by order, in the incoming fields. The directionality of the signal (phase matching) stems from the fact that the sample is much larger than the optical wavelength. The opposite limit holds in NMR, and the signal is thus isotropic. However, the directional information may be retrieved by modifying the phases of the pulses (phase cycling). Phase cycling in optical measurements was demonstrated experimentally by Warren Warren. The effective Hamiltonian necessary for optical 2D simulations is complex and requires extensive electronic structure calculations. In contrast, the spin Hamiltonians in NMR are known and universal, greatly simplifying the simulations and analysis of signals. The dipole moments in NMR are aligned in parallel by the strong magnetic field. The specific orientations of infrared dipoles contain useful structural information that can be retrieved by varying the pulse polarizations. NMR has a remarkable structural resolution unmatched by optical signals. However, the latter provides a different window with complementary information. A purely classical simulation protocol for nonlinear response was developed in 1996 with Vadim Khidekel and Vladimir Chernyak.

Liouville space pathways provide an intuitive picture for interpreting the optical response; the various contributions are fully time-ordered, and dephasing processes can be readily investigated. Coherent ultrafast spectroscopy in the visible and infrared regime is described using nonlinear response functions expressed as combinations of multitime correlation functions of the dipole operator. They carry all the relevant molecular information and offer a compact description of a broad range of nonlinear spectroscopies which differ by the temporal sequences of pulses as well as their frequencies and wave vectors. Liouville space pathways can be depicted using double-sided Feynman diagrams. Measurements with partial control over time ordering can be described using complementary loop diagrams, which were developed starting in 2008 by Christoph Marx, Oleksiy Roslyak, and Saar Rahav.

Strategies for the design of pulse sequences in coherent vibrational and electronic spectroscopies that accomplish the same goals as multidimensional liquid or solid state NMR through the control over coherence transfer pathways but on much faster time scales were established. We demonstrated how resonant femtosecond four-wave mixing may be used to directly probe electronic correlation effects using the photon-echo pulse sequence with reverse time ordering. Together with Lijun Yang and Rafal Oszwaldowski, we proposed in 2007 a double quantum coherence pulse sequence, and showed that such signals are induced by electron correlations, providing a background-free measure of electron correlations and allowing certain projections of many-body wave functions to be visualized. This approach has great promise for the study of strongly correlated boson and fermion systems.

The fundamental connections between nonlinear spontaneous fluctuations and response functions were established using the Liouville space approach by Adam Cohen in 2003 and used to develop a dynamical theory for intermolecular forces between optically driven molecules under nonequilibrium conditions and in dissipative environments. Adam had further shown how to predict measurements that probe the response of spontaneous

fluctuations to impulsive excitations using superoperators in Liouville space. These form the basis for the generalization of fluctuation dissipation relations to the nonlinear regime. Oleksiy Roslyak had further developed this approach for predicting new classes of experiments which involve both classical and quantum modes of the radiation field.

Several protocols including the cumulant expansion of Gaussian fluctuation (CGF), a quasiparticle scattering approach, the stochastic Liouville equations (SLE), and direct numerical propagation were developed for the simulation of multidimensional signals of vibrational and electronic excitons. These are implemented in a code SPECTRON that interfaces with standard electronic structure and molecular mechanism MD codes. The code was put together by Wei Zhuang and Darius Abramavicius by combining earlier codes. Chirality-induced techniques which dramatically enhance the resolution were demonstrated. Recent advances in pulse-shaping technology allow the multiparameter design of optical pulses through the optimization of pulse shapes, phases, durations, intervals, and frequencies to achieve desired goals. Dimitri Voronine and Darius Abramavicius had used genetic learning algorithms to provide closed feedback loops for the design and the simplification of multidimensional signals. By combining pulse shaping with coherent control learning algorithms, pulse shapes can be designed to achieve desired spectroscopic targets, such as the selective elimination or enhancement of cross-peaks in order to improve the resolution, manipulating the line shapes of various peaks to achieve narrowing in specific directions, and minimizing vibrational decoherence rates.

Cooperativity in the nonlinear optical response of chromophore aggregates is a fascinating issue. I had first worked on this when approached by Annabel Muentner, a senior scientist with tremendous insight at Kodak Research Laboratories in Rochester, to address superradiance, enhanced collective spontaneous emission in J aggregates. It has been a pleasure to collaborate with Annabel who was a worldwide leader in the field of photophysics of chromophore aggregates. This effect was first predicted for an assembly of absorbers by Dicke. The N atoms in the ensemble act like a giant dipole, enhancing the radiative decay rate by factor N . This issue was of some concern to Kodak, since the primary event in color photography involves the injection of charge from photoexcited J aggregates of cyanine dyes into silver halide particles. Superradiance is a decay channel that competes with the charge injection and can limit the efficiency of the photographic process. Kodak scientists were interested in minimizing it; to me, it was much more exciting to find conditions where cooperativity can be maximized. Whatever the goal, it requires understanding the factors that control the coherence size. This is a nice illustration of how basic and applied research can coexist despite opposite objectives. With a postdoc, Frank Spano (1989), we have shown how thermal dephasing affects these processes. Douwe Wiersma was later able to observe ~ 100 -fold enhancement of the radiative decay rate in J aggregates at low temperatures.

Spano was working on cooperativity in the nonlinear optical susceptibilities of aggregates. During the same period, considerable effort was being focused on developing optical materials with large off resonant nonlinear susceptibilities, which had numerous implications on the sensitivity of molecular and semiconductor devices. Predictions made in the literature were that aggregates made of N chromophores $\chi^{(3)}$ should have a signal that grows as $\sim N^2$. If true, this could offer a path for great enhancements.

Despite considerable effort, experiments had failed to observe such enhancement. With Spano (1989), we showed that the mystery can be resolved by a careful analysis of Liouville space paths. It turns out that there are two groups of paths: One scales as $\sim N^2$ and the other as $\sim N(N-1)$. The two have opposite signs and in the off resonant regime interfere destructively to yield an overall $\sim N$ scaling. All cooperativity is lost! Two disturbing aspects of this observation are that it is difficult to obtain physical insight from individual pathways, due to these massive cancellations. All pathways must be carefully added first. This also causes difficulties in calculations, since numerical accuracy is reduced. For me, this raised the interesting issue: Is it possible to reformulate the problem so that these interferences will be built in from the outset, thus making the calculation more intuitive? We found that by calculating the response using equations of motion rather than sums over global states we recover the N scaling in a straightforward and highly intuitive way. The deeper insight of this is that equations of motion map the system into a collection of classical anharmonic oscillators. The thinking in terms of oscillators rather than global eigenstates offers wonderful new insights. The optical nonlinearities then originate from the scattering of quasiparticles, which connects with many-body theories in a profound way. It triggered the development of the nonlinear exciton equations and quasiparticle expressions for various nonlinear signals. It was also crucial for the 1993 work with Tanimura on multidimensional Raman spectroscopy of vibrations in liquids which were modeled as oscillators. The connection between the sum over states and the oscillator pictures was later established by Vladimir Chernyak and is discussed in my 2008 paper with Oszwaldowski and Abramavicius. Starting in 1989, Jasper Knoester was working on the interpretation of pioneering transient grating experiments by Mike Fayer in molecular crystals. These four-wave mixing experiments turned out to reveal polariton (rather than the anticipated exciton) transport. Using modern terminology, polaritons are entangled states of photons and matter. Jasper further demonstrated how intermolecular forces in crystals may be formulated in terms of the exchange of polaritons and provided an elegant formulation of the local field problem in nonlinear optics.

I was intrigued by the completely different approaches taken by physical chemists and condensed matter physicists to electronic structure problems. To bridge the gap and connect the two communities, we have developed a quasiparticle density matrix representation of electronic excitations by recasting the time dependent Hartree–Fock (TDHF) and the time dependent density functional (TDDFT) equations in terms of the single electron density matrix in Liouville space. A collective-oscillator, quasiparticle, representation of the density response of many-electron systems which explicitly reveals the relevant electronic coherence size was developed. Closed expressions for the nonlinear density–density response were derived, eliminating the need to solve nonlinear integral equations, as required in the Hilbert space formulation of the response. Electronic excitations in assemblies of conjugated molecules were calculated by following the time evolution of the reduced single-electron density matrix and mapping the electronic motions onto a set of coupled collective electronic oscillators (CEO). These “electronic normal modes” are then used to develop a real space chemical intuition by relating the dynamics of electronic charges and coherences directly to the optical response, without ever introducing the many-electron molecular eigenstates. The scaling and

saturation of nonlinear susceptibilities with molecule size were interpreted by identifying the dominant electronic modes and anharmonic couplings. This approach bridges the quasi-particle electron–hole semiconductor picture and the real-space representation of chemical bonding, and suggests extensions of density functional techniques to include electronic coherences in addition to charges as the functional variables. We used it to analyze linear and nonlinear optical properties of conjugated molecules and semiconductor particles. Sergei Tretiak and Vladimir Chernyak were instrumental in these developments which started with the work of Akira Takahashi in 1994 and later Guanhua Chen. Vladimir Chernyak who has closely worked with me for eight years has an extraordinary clear vision and unusual mathematical talents. He has greatly advanced the Liouville space approach to many-body and exciton systems.

Dendrimeric molecules with branched tree-like structure show unusual transport and optical properties, stemming from their peculiar dimensionality: The connectivity between different sites is one-dimensional, but the number of atoms grows exponentially with generation, as in infinite-dimensional systems. Raoul Kopelman and Yosi Klafter independently explored the applications of dendrimers for funneling energy and optimizing the quantum yield of desired photochemical channels. The nature of these excitations and their scaling with molecular size were predicted. The funneling and localization properties of photogenerated electron–hole pairs in several families of dendrimers were related by Tretiak and Chernyak to the molecular connectivity and shown to be responsible for the scaling of optical and transport properties with the number of generations. An important consequence of that study was the ability to dissect the electronic excitations of dendrimers into distinct chromophores, despite the delocalized nature of the underlying electronic states. The approach provides a natural framework for the design of supramolecular structures such as artificial light-harvesting antennae with controlled energy funneling pathways, and allows exploring the coherent coupling among different segments. A fruitful collaboration on these effects in paracyclophane-based aggregates was developed with Gui Bazan, Joseph Zyss, and Norbert Scherer.

I had moved from Rochester to UC Irvine in 2003. Tomoyuki Hayashi, Ravindra Venkatramani, Wei Zhuang, Andy Moran, Thomas La Cour Jansen, Yuki Nagata, and Cyril Falvo had developed new simulation algorithms for two-dimensional infrared (2DIR) techniques. Darius Abramavicius, Dimitri Voronine, and Frantisek Sanda had continued the development of 2D electronic techniques for studying exciton transport in photo-synthetic complexes. Two review articles which appeared in 2009 summarize these developments. One in *Chemical Reviews* by Darius Abramavicius, Benoit Palmieri, Dimitri Voronine, and Frantisek Sanda covers 2D electronic spectroscopy, and the other in *Angewandte Chemie* by Wei Zhuang and Tomoyuki Hayashi covers the 2DIR work and continued to explore how multi-dimensional techniques can be further extended to higher frequency regimes. A 2009 special issue of *Accounts of Chemical Research* on multidimensional spectroscopy co-edited with Peter Hamm and Yoshitaka Tanimura provides an overview of the field.

The design of two-dimensional ultraviolet signals in proteins and other systems is one focus of my current research. This direction has been pursued by Zhenyu Li, Jun Jiang, and Darius Abramavicius. We calculated two-dimensional chiral ultraviolet spectra of proteins and extended the Liouville space formulation to resonant attosecond nonlinear ultrafast X-ray spectroscopies,

in anticipation of the development of new X-ray sources, both the free electron laser and table top high harmonic generation. X-ray pulses have the unique capacity to detect nuclear and electronic motions with high temporal and spatial resolution.

The advent of lasers delivering femtosecond optical and infrared pulses in the 1980s has allowed the study of dynamical processes on the time scale of atomic motions in molecules, liquids, solids, and biological systems. Pump–probe spectroscopies as well as a rich diversity of coherent multiple-pulse nonlinear techniques are possible. Optical techniques view the dynamics through their projection on the dipole moment. As such, they are subjected to selection rules and only provide an indirect and partial picture of the dynamics. A more direct and complete observation of nuclear and electron motion may be achieved through the combination of the high temporal resolution of femtosecond laser spectroscopy with the atomic-scale spatial resolution of structural techniques such as X-ray diffraction and X-ray absorption, which look directly at the motions of charges.

Ultrafast picosecond to attosecond sources of X-rays are revolutionizing the study of elementary electronic and vibrational processes, much like what happened with femtosecond lasers approximately 20 years ago. These advances open up new possibilities to carry out nonlinear spectroscopic studies of atoms, molecules, gas phase systems, and condensed-phase materials in the X-ray region with high temporal and spatial resolution. Multiple core hole excitations provide novel probes for valence electron motions. The Liouville space formulation of optical spectroscopy was extended to develop a systematic theoretical framework for the description and computation of resonant nonlinear ultrafast X-ray spectroscopies (pure X-ray and mixed optical/X-ray techniques). Our early work on the topic started in 2001 with Satoshi Tanaka and continued with Igor Schweigert in 2008 and later by Daniel Healion. While considerable worldwide effort has been placed on time resolved diffraction of X-rays or femtosecond electrons (by Ahmed Zewail and Dwayne Miller), our work focused on resonant multidimensional core hole spectroscopy that provides information on electron coherence, going beyond the charge density alone.

Correlation function expressions of charge and current densities provide a unified treatment and classification of the information content of various possible techniques and connect them with their optical counterparts. New possibilities for looking at electron–electron correlations and the flow of charges were proposed. X-ray pulses have the unique capacity to directly probe structural fluctuations, nuclear motions, and relaxation processes, as well as the dynamics of elementary excitations in materials, such as excitons, polaritons, and polarons in real time and space. Purely X-ray nonlinear spectroscopies, such as pump–probe, multiwave mixing, and time and frequency resolved emission spectroscopy are possible.

One technique I find particularly promising is stimulated Raman with short attosecond X-ray pulses. A Raman process with X-rays prepares wave packets of valence electronic excitons in the same manner that femtosecond pulses in the visible prepare vibrational wave packets. The entire manifold of valence electronic excitations may be monitored by multidimensional broad band X-ray techniques. Multiple pulse X-ray measurements combine various aspects of my work over many years: multidimensional spectroscopy, the quasiparticle approach, and the many-body physics of quasiparticles. There is a common

thread going from the NMR to the infrared, visible, ultraviolet, and eventually X-rays.

Another wide open future direction in the horizon is performing nonlinear optical measurements on complex molecular systems by utilizing the quantum nature of the optical field (photon counting and entanglement). Nonlinear spectroscopy is most commonly performed using classical coherent fields. Quantum fields are manipulated with breathtaking achievements for quantum information applications. These applications usually keep matter off resonant or use simple atoms. The basic experimental schemes are yet to be developed. This direction has been pursued by Oleksiy Roslyak and Marten Richter.

Together with Saar Rahav, we had discovered great insights by looking at optical signals such as CARS from the molecular as opposed to the field perspective. My group is working on combining the superoperator Liouville space formalism with many-body theory. These are integrated into an intuitive set of tools that can be used by theorists and experimentalists for calculating electronic and vibrational dynamics in complex molecules and predicting their signatures in novel spectroscopic probes. Computing response functions by following the time evolution of superoperators in Liouville space offers an attractive alternative to the diagrammatic perturbative expansion of many-body equilibrium and nonequilibrium Green's functions. The bookkeeping of time ordering is naturally maintained in real (physical) time, allowing Wick's theorem to be extended to superoperators, and the development of new approximation schemes and reduced descriptions of molecular events. This work is summarized in a 2008 physics report article with Upendra Harbola. Electric current distributions and current-induced fluorescence in molecular junctions and methods for their analysis in real space and real time were developed by Jeremy Maddox and Upendra Harbola. Various measures of photon counting statistics in single molecule spectroscopy were calculated. Quantum effects in the distribution of work and entropy production in nonequilibrium steady states (the fluctuation theorem) have been explored by Massimiliano Esposito and Upendra Harbola.

In the course of my education, I have greatly benefitted from attending international schools. For European students, this is quite common, but it is much less so in the U.S. I had discussed this need with Rudy Marcus, and we organized two Gordon-Kenan Chemical Physics Summer School Programs. The First School on Analytical Approaches to Rate Processes and Time-Resolved Spectroscopy in Condensed Phases was held in 2000. The Second School on Many Body Techniques in Chemical Physics was held in 2002. One issue we emphasized was training theory students in analytical techniques in addition to computer skills. This initiative was stopped upon my moving to UCI. I am glad that it has been now revived in the summer program at Telluride.

Over the years, I have enjoyed steady support from several agencies. NSF has funded my research throughout my 30 year career. NIH has supported the development of multidimensional spectroscopy for biomodels, and DOE has supported the attosecond X-ray work. Other agencies, including AFSOR, ONR, the US Army, and PRF, have supported my efforts as well. Striking a good balance between the most creative, curiosity driven, single investigator grants and larger collaborative efforts has been a challenge. The freedom allowed by these agencies to not stick to the original plan, enabling exploration of new directions as they come along, is highly valuable.

It has been a great privilege to work over the years with so many talented students, research associates, and colleagues. I am grateful to all of them. I cannot think of anything more rewarding than seeing theoretical predictions realized experimentally. In 1928 (or so), the British astrophysicist A. Eddington (who experimentally proved Einstein's general theory of relativity) stated: "No experimental result should be accepted before being confirmed by theory". I am indebted to Debra Haring who was my assistant for many years in Rochester. Last but not least, I am thankful for the tremendous support from my understanding wife Dana and sons Eran and Ronen.

Shaul Mukamel