

## Tribute to James L. Skinner



Photograph taken by April Leslie

This special issue of *The Journal of Physical Chemistry B* is in honor of Jim Skinner's numerous scientific accomplishments throughout his career. His work has broadly impacted both theoretical and experimental physical chemistry. A central theme of his work is understanding how spectroscopy can be used to learn about structure, dynamics, and energy flow in complex systems. His research has guided the interpretation of optical and vibrational spectroscopy in a diverse range of contexts, from crystalline and amorphous solids to liquids and biological systems. In the paragraphs that follow, we highlight chronologically just a few of his many scientific contributions.

From the mid 1980s through the early 1990s, Jim's research focused on understanding optical and vibrational spectroscopy in solids, for which molecular-level spectroscopic detail is often masked by inhomogeneous broadening—especially in amorphous materials. Experimental advances, such as photon-echo and hole-burning spectroscopy, were making it possible to deconvolute the effect of local molecular dynamics and interactions (homogeneous broadening) from the inhomogeneously broadened spectrum; however, an adequate theoretical framework through which to interpret these results was lacking. The standard theoretical approaches for such systems at the time were based on second-order perturbation theory, where the width of a homogeneously broadened spectral line was controlled by population relaxation. This “weak-coupling” limit was unsuitable for many condensed phase systems. During this period, Jim and his group made ground-breaking advances in the development of higher-order or

nonperturbative approaches that were applicable in the strong-coupling regime relevant to most systems of experimental interest. These basic ideas were also extended to examine proton transfer in crystals—a chemical version of the classic spin-boson problem.

The relaxation of coherent spectroscopic excitations in condensed media can be described in two components: population relaxation (the return to the equilibrium ground and excited state populations) and dephasing (the loss of phase coherence between the ground and excited states). The relaxation times for these two phenomena are given by  $T_1$  and  $T_2$ , respectively. The dephasing time has a component that is directly tied to  $T_1$  plus an additional component referred to as “pure dephasing”. In the standard second order theory, the pure dephasing component is due entirely to the modulation of the energy level spacing through interactions with the environment (“diagonal coupling”) and is independent of the population relaxation. This leads to the important inequality  $T_2 \leq 2T_1$ , which is used extensively in interpreting spectroscopic experiments, despite the fact that it is rigorously true in only the weak-coupling limit. Jim and his group were able to extend the existing theories of spectroscopic relaxation to infinite order in the absence of population relaxation (diagonal coupling alone) and to fourth order for the general case (both off-diagonal and diagonal coupling). One notable result of the fourth-order extension is the observation that under specific circumstances it is possible for  $T_2$  to be greater than  $2T_1$  in direct contradiction to the usual inequality given above. Jim's extensions of the theory of relaxation in vibrational and optical spectroscopy have become important tools in the interpretation of experiments and invaluable baselines for further theoretical development.

During this time, Jim also made important advances in understanding and interpreting hole-burning spectroscopy in amorphous materials. For such systems, hole-burning spectroscopy is a popular technique to probe the details of inhomogeneously broadened spectra through the use of a laser to bleach out a narrow region of the spectrum. Experiments show that these spectral “holes” are both broadened and shifted with external stress (pressure or electric field) is applied, as the accidental degeneracy of different local environments is lifted by the stress. A simple, but elegant, statistical theory of this stress-induced broadening developed in the Skinner group put these experiments on a strong molecular footing. The theory's prediction that the broadening of the hole is linearly dependent upon the hole burning frequency was later confirmed by experiment.

In the mid 1990s, Jim turned his attention from solids to liquids. Jim was an early leader in the calculation of accurate vibrational relaxation rates within liquids. Such relaxation processes play a crucial role in reaction dynamics because they provide pathways to dissipate excess reaction energy into the rotations, translations, and vibrations of the surrounding solvent. Although the basic theoretical framework for calculating

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relaxation was established much earlier (and follows simply from Fermi's golden rule), the resulting formulation requires calculation of a *quantum mechanical* time correlation function that can differ by orders of magnitude from the corresponding *classical* correlation function when evaluated at typical vibrational frequencies. Jim showed that the former could be approximated in terms of the latter by proper application of so-called quantum correction factors. Although the choice of correction factor is not without ambiguity, Jim showed that, for a diverse set of cases, such an approach could be used to calculate vibrational energy relaxation rates often to within an order of magnitude of the observed experimental results. This work provides a beautiful picture of the time scales and pathways of energy flow in the condensed phase.

Over the last 15 years, Jim's major research focus has turned to vibrational spectroscopy of condensed phase systems with particular emphasis on liquid water and aqueous solutions. Due to the sensitivity of a chromophore's vibrational frequency (and sometimes vibrational intensity) to its chemical environment, the vibrational spectrum serves as a probe of both structure and dynamics. Modern ultrafast nonlinear vibrational spectroscopy experiments allow the evolution of this vibrational energy gap to be probed on femtosecond to picosecond time scales. Here, Jim was one of the pioneers in bringing together information from molecular-dynamics simulations and electronic structure to facilitate quantitative modeling, analysis, and interpretation of these complex experimental observables in terms of concrete molecular structure and dynamics, often in collaboration with leading experimentalists such as Michael Fayer, Andrei Tokmakoff, and Martin Zanni.

On the basis of these ideas, Jim has made a particular impact in our understanding of the dynamics of water. Using a mixed-quantum classical approach that combines standard molecular dynamics simulations with a configuration-dependent "map" of the vibrational frequency and intensity (derived on the basis of electronic structure calculations), he was able to reproduce IR adsorption line shapes over a wide range of conditions as well as complex nonlinear photon-echo and 2DIR experiments. This work was later extended to examine the air–water interface, modeling surface-sensitive sum frequency generation (SFG) experiments. There, Jim helped resolve significant controversies regarding the structure of this ubiquitous interface as well as the corresponding origin of the low-frequency peak in the SFG experiment. He showed that this spectral feature arises due to three-body interactions (due to cooperativity/anticooperativity in hydrogen bonding) and is not consistent with ice-like ordering at the liquid surface.

Beyond liquid water, Jim has made major impacts in the application of vibrational spectroscopy to systems of biological relevance and the interpretation of the corresponding experimental results. Jim extended the "mapping" approach to peptides (with the amide I stretch serving as the chromophore) and used this approach to study a wide range of biologically important systems, including the influenza M2 ion channel, amylin aggregates, membrane proteins, and urea/water interactions.

Over the last 30 years, Jim has mentored 26 Ph.D. students and 14 postdocs, many of whom are now actively working as professional scientists, including many at research universities, national laboratories, and liberal arts institutions. Speaking on behalf of all of Jim's former mentees, we sincerely thank Jim for his scientific and personal guidance through the years; his influence on our lives has been profound. The breadth of articles

in this special issue is a clear testament to his immense impact on physical chemistry throughout his career. We wish Jim the very best and look forward to his continued contributions.

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