Photograph courtesy of Tyagan Miller

Scientific Contributions of Charles S. Parmenter

We pay tribute in this volume to Professor Charles S. Parmenter, whose scientific contributions in the field of primary photophysical processes, intramolecular dynamics, and inelastic collisional energy exchanges in free polyatomic molecules span an active research career extending over 40 years. These contributions have been influential, seminal, and elegant both in their style and precision.

Following his Bachelor's course at the University of Pennsylvania in Philadelphia, Charlie (as he is known to his innumerable friends) moved in 1958 to work for his doctorate at the University of Rochester under the direction of W. A. Noyes, Jr., one of the leading figures in molecular photochemistry. This was followed by 2 years as a postdoctoral fellow at Harvard University in association with G. B. Kistiakowsky. These formative years were to determine the direction of his research for the rest of his career. In 1964, he arrived at Indiana University in Bloomington as an Assistant Professor in the Department of Chemistry. Indiana University has been his home ever since.

In hindsight, the late 1960s can be viewed as an exceptionally interesting time in the development of physical chemistry. The reduction of time-independent macroscopic structural chemistry to the microscopic molecular physics of bonded atoms-in-molecules (the precisely determined geometries of molecules and the elastic properties of their bonds governing their vibrational motions) was largely complete. Even the quantum mechanical electronic structure of chemical bonding was becoming accessible through spectroscopy and computational simulation. But the next step, the microscopic description of time-dependent molecular change in the course of a chemical reaction, was still largely unresolved. The classical era of gas-phase kinetics of "simple" reactions, either uni- or bimolecular, had led to postulated mechanisms that were almost always more complicated than reactants (such as hydrogen and oxygen) and products (such as water) might reasonably have led one to expect.

The language of the time was of "activation energies", "transition states", "the reaction coordinate", "reactive short-

lived intermediates" such as free radicals, and the "elementary reactions" successively involved in the overall transformation. As the essential activation energies were usually thermal, theories were statistical and characterized by constraints on the partition of molecular kinetic and internal energies, particularly in the vibrational degrees of freedom. It was not easy to see the way forward, and one recalls a review of the field in a college text that concluded that the only simple reactions remaining were those that had not yet been closely examined.

One way to beat Boltzmann's demon was through photochemistry. Chemically significant activation energy can be injected into the reactant molecules in precisely defined quantities at time zero so that the evolution of the system could be followed in "real time". Such experiments contain two parts. The first involves the primary unimolecular photophysical processes associated with photon absorption and the subsequent dissipation of the energy out of the excited state(s) initially populated. Unlike diatomic molecules having only two possible channels for energy dissipation (fluorescence or dissociation into atoms), polyatomics of even quite modest size can have many channels. The language here is that of the Jablonski diagram with labels such as E (electronic), S (singlet), T (triplet), V (vibrational), and R (rotational). The second part is everything that happens at and after the first collision between the excited molecule and its environment. Since both parts determine the final products, both have to be understood. Each in turn involves separate E−V−R processes characterized by rate constants covering an enormous dynamic range of magnitudes. The experimental challenge is immediately obvious: how to separate the processes, particularly those of the first (unimolecular) type from those of the second (bimolecular) type, and how to measure their specific rates.

It is to these fundamental problems and the associated experimental challenges that Charles Parmenter has devoted his professional attention. Leading in importance is the choice of molecules. First, they must have discrete visible or accessible ultraviolet absorption spectra. Second, they should be of sufficient size to present a palette of processes typical of polyatomic molecules as a whole but small enough to have spectra that can be analyzed in terms of their fully state-resolved E−V−R structures. Third, they must have excited states that fluoresce, for it is through the details of its fluorescence spectrum, in both the time and frequency domains, that the molecule reports back on what is happening to it after it absorbed the exciting photon at time zero. Fourth, the fluorescence efficiency has to be sufficiently high for the emission to be experimentally detectable: here, as in the rest of spectroscopy since its invention, the problem is that of being "photon-challenged" (as Charlie puts it).

These requirements present severe constraints on the choice of molecular prototypes. In the event, the three molecules that appear again and again in the Parmenter bibliography of publications are glyoxal (four decent atoms), benzene (six) and *p*-difluorobenzene (pDFB, eight). But the greatest of these is benzene (to which the other members of the International Brotherhood of Benzenologers will unhesitatingly attest). Its size quickly generates huge densities of states with increasing energy above the ground state. Its chemistry generates large numbers of local potential minima on its ground-state potential surface, usually called valence isomers, opening the way to the chemistry of intramolecular isomerization. But its high symmetry and rigidity factorize the total problem into well-separated blocks that can be selectively accessed (e.g., by electric dipole selection rules, making it tractable as a sum of separable simple harmonic oscillators ("the only diatomic molecule with a 6-fold axis of symmetry")). Last, its electronic structure is the prototype of aromaticity, one of the testing grounds of valence theory.

And so one of the first problems to be tackled was that of the primary photophysical decay processes in the S_1 state of benzene itself, the one responsible for the famous 2600-Å absorption system in the near-ultraviolet and its associated fluorescence. These spectra were well known, but their study had never managed experimentally to reach the collision-free regime. To increase intercollisional periods to lengths greater than the fluorescence lifetime ($\sim$10 ns) required pressures so low that the fluorescence had become too weak to observe with the detectors then available. The fluorescence (Channel 1) was also not resonance fluorescence: although the excitation from the intense 2537-Å line of mercury was into some ill-defined vibrational level(s) well above the zero point of S_1, the emission was that of vibrationally thermalized S_1. Moreover, part of the quenching was due to the transfer of excitation into the lowest triplet state (T_1) of benzene, intersystem crossing (ISC, Channel 2), which is well known in condensed phases. The quantum yield of fluorescence was less than unity, but what did the quenching? Collisions? Toward the end of his stay at Harvard, Charlie constructed an apparatus that made it possible to measure the fluorescence at the required very low pressures and, moreover, in dispersed form showing the vibrational band structure of the fluorescence.

The results were convincing. The spectrum observed was the resonance spectrum. The fluorescence quantum yield is less than unity, and S_1-T_1 ISC occurs even in the free molecule under collisionless conditions. The natural lifetime of the triplet state under these conditions was moreover orders of magnitude shorter than in condensed phases, presumably by unimolecular nonradiative transition to the ground state, S_0. How could this be? How could a free molecule in one electronic state spontaneously interconvert into another? Under the "crude Born−Oppenheimer approximation," the electronic transition is itself totally forbidden by symmetry. But taking into account vibronic coupling in the adiabatic approximation (i.e., Herzberg−Teller coupling in which electrons instantly rearrange themselves in response to the displacement of the nuclei from their equilibrium positions), the transition becomes allowed provided there are odd changes in the quantum numbers of at least one nontotally symmetric vibration. And this theory had been spectacularly successful in accounting for almost every detail of the observed band structure of the spectrum. Here was prima facie evidence for the importance of yet further items of theory neglected in the adiabatic approximation (spin−orbit coupling included). These items were finally provided in the classical article by Bixon and Jortner in 1968. An isolated polyatomic molecule can act as its own heat bath.

Since early experimental efforts at Indiana to assign vibrational structure in the spectrally resolved resonance fluorescence obtained from benzene under collisionless conditions utilized Hg 2537-Å excitation, a detailed understanding of the excited-state vibrational level(s) being initially populated was needed. These excited vibrational levels were identified with George Atkinson through an extensive reexamination of the well-known 2600-Å benzene absorption spectrum using both new absorption data and revised vibrational mode assignments.

The next step involved moving away from the restrictions of 2537-Å excitation and was taken in association with Mike Schuyler. There were two parts. The first was the generation of grating-tunable, narrow-band ultraviolet fluorescence excitation radiation. Individual vibronic levels in S_1 could be selectively

excited band by band in the absorption spectrum. The second was the new technique of time-gated single-photon detection that was sensitive enough to plot out the now dispersed but very weak fluorescence spectrum. Thus was born single vibronic level (SVL) fluorescence, one of the Parmenter group's most seminal and lasting contributions. There were two immediate applications. The first showed that the vibrational structure of the fluorescence spectrum depended on the excited-state vibrational mode being populated; it could then act as a powerful tool for spectroscopic assignments. (In a molecule as large as benzene, this is no trivial task!) The second was to show that the relative fluorescence lifetimes and quantum yields also depended on the excited-state vibration being populated. The extreme manifestation of the latter dependence is the sudden onset, at about 3000 cm^{-1} above the zero point of S_1, of yet another radiationless intramolecular relaxation process into other electronic states that occurs so fast that it now totally quenches all fluorescence. This famous Channel 3 has a mechanism that is still not fully understood. (Its overall course is one of S_1-S_0 interconversion (IC) at a rate so high that it bypasses S_1-T_1 ISC. Both it and ISC are governed by details of vibrational excitation analogous to Franck−Condon factors.)

Having experimentally descended to the limit of collisionless photophysics, it was a natural step for the Parmenter group to reverse the process and watch the relaxation of the fluorescence from the resonant vibronic state to a thermal distribution by the addition of increasing pressures of an added gas. This opened a whole new field: the study of fully state-resolved collisional bimolecular vibrational-energy transfer. The collisional cross sections now also depend on the vibrations being excited. Working with Kenneth Tang, the Parmenter group clearly identified many of the regularities characterizing the general state-to-state propensity rules.

The advent of tunable lasers then made it possible to spectrally narrow the excitation of electronic states to the resolution of single rotational levels. The workhorse was now glyoxal, and so (with Berchtold Rordorf) was born the field of single-rotational-level (SRL) fluorescence measurements, with its extension to the measurement of bimolecular rotational state-to-state collisional-energy transfer.

But what happens to a molecule in an excited state immediately after the absorption of a photon? The absorption does not excite a vibrational stationary state. Consequently, as the molecule begins to vibrate, its motion becomes a mixture of more than one harmonic component (normal mode), namely, through so-called intramolecular vibrational redistribution (IVR). IVR in polyatomics is on the time scale of vibrational periods (i.e., femto- to picoseconds) and cannot be followed in real time with pulsed excitation sources such as lasers with nanosecond time resolution. But once again, the process can be detected by effectively disturbing it, such as by quenching it after shorter

and shorter times following photon absorption (time zero). And the way Charlie suggested that this could be done was by adding a gas such as oxygen, thereby removing the excited molecule chemically and shortening its lifetime controllably into the realm of picoseconds by simply increasing the pressure of the quencher (i.e., chemical timing). Under such quenching conditions, it does not matter at what instant in the course of an exciting irradiation the molecule absorbs the photon but only how long until the first collision effectively destroys the optically populated state. The effect is seen in the fluorescence. In this way, IVR time scales could for the first time be measured directly in real time, and their dependence on vibrational excitation could be plotted. The molecule examined in these studies with Karl Holtzclaw was pDFB.

The final and most recent step is to take energy resolution down to that of translation. This has been done by forming a beam of state-selected (E−V−R) molecules such as glyoxal and crossing it with a beam of collision partners T (work with Douglas Krajnovich). The use of a molecular beam cooled by adiabatic expansion at a nozzle is another powerful way of beating Boltzmann's demons. The inelastic scattering is revealed in the fluorescence of the emerging beam. Vibrational- and rotational-energy transfer not attainable by other methods is studied in detail. One conclusion to emerge is that the cross sections depend much more on the incident kinematics than they do on the intermolecular potentials.

There is much, much more that could be told, but the Parmenter record speaks for itself. It may seem that the range of topics within the wider field of the whole of physical chemistry covered by Charles Parmenter and his group at Indiana is a rather narrow one, but therein lies its virtue. The simple photochemistry of nearly half a century ago to the highly detailed and sophisticated chemical physics of molecular dynamics studied today represents an exceptionally broad series of experimental and theoretical challenges. Each step was built on the one that went before, and to each step, Charlie made fundamental contributions of great imaginative and experimental virtuosity. His changing group of students and collaborators, nearly 50 of them over the years, was at any time never very large: almost half of his publications have only one coauthor. With his typical modesty, Charlie will claim that it was they who did it all. Perhaps, even if unlikely. But that is Charlie. In any event, there was always someone who knew what to do and why it was significant to undertake it. Most importantly, there was always someone who provided the inspiration and the enthusiasm needed to motivate many different individuals over almost half a century. And there is no doubt that this someone was also Charlie.

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John H. Callomon