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CENTENNIAL FEATURE ARTICLE

Interaction between Experiments, Analytical Theories, and Computation[†]

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This article is a summary of a talk given at the ACS Centennial Symposium in Physical Chemistry in Philadelphia in 2008, updated with more recent studies. In keeping with the spirit of the symposium, the article is in part historical and in part a review of the newer research. The talk was divided into two parts, the first on different isotopic effects in chemistry, including the mass-independent fractionation phenomenon in gases and H/D isotope effects in enzymes, and the second on two different surface phenomena, "The Bad and the Good". The "Bad" is the fluorescence intermittency of semiconductor nanoparticles, (quantum dots, QD) being an unwanted feature in sensor applications. The "Good" is the "on water" catalysis of organic reactions, a mode of green chemistry. The possible role of Auger-type mechanisms in trapping and detrapping in the QD and hence in the formation of dark and light periods is explored. Some suggestions are made on the novel "breakpoint" phenomenon discovered for H transfer in a thermophilic enzyme.

Introduction

One might well and should ask what have we learned from theory and how does theory help to design and interpret experiments. For example, what has electron transfer theory taught us about the early steps in photosynthesis? What has nature done to permit it to utilize solar energy to form an ion gradient across a membrane that can be used for the production of energy-rich molecules? What are the problems permitting the forward electron transfer to occur rapidly in the photosynthetic primary steps instead of wasteful back reactions? What has theory taught us about the nature of the environment of the primary species that permits it to make this energy conversion? These questions are all addressed and largely answered by theory.

Or again in atmospheric and combustion reactions, what has theory taught us about the various and many reactions steps, even using simple statistical ideas to treat the individual reactions in these systems? What experiments interpreted by theory have provided information on the validity of statistical theory? This topic is among those referred to in the current paper.

What have we learned from single molecule studies of fluctuations in proteins and their relation to catalytic activity? These studies have revealed the importance of slow motions in the millisecond to second scale, a property also studied by earlier bulk dielectric dispersion investigations. Have we learned something specific about what causes these slow motions? Are they caused by major conformational changes or intricate rearrangements of hydrogen-bonded structures? Are more specific techniques directed toward relations between one part of the protein and another needed to supplement such single molecule studies in order to really see what is going on in these slow fluctuations?

In the field of surface phenomena, what have we learned from the surprising on-water catalysis of some organic reactions? How can we predict when they occur and what the nature of the stereochemistry is? Or in another area where surface effects are important, what has theory taught us about how quantum dots function and what their potentialities for applications may be?

In addition to the fundamental understanding of important systems there is also sometimes a serendipitous application to societal problems. Only a few of these questions will be addressed in the following, but at some point a thoughtful examination would be desirable. We begin with several areas where isotopes have played a key role.

Isotope Effects

1. Electron Transfer Reactions. Isotope effects have played a major role in many branches of chemistry. Our involvement has been several-fold: in isotopic exchange reactions in inorganic chemistry, known also as self-exchange reactions, radioactive isotopes were used as tracers. The many experimental results led to the writer's electron transfer theory in 1956.[1] This development began with Libby's application of the Franck–Condon principle to explain why some of these self-exchange reaction were slow and others fast.[2] He reasoned that if a reactant underwent a large change in bond lengths in changing from one redox state to another, as in the reaction of $Co(NH_3)_6^{+2}$ to form $Co(NH_3)_6^{+3}$, each new product ion would be formed in a very unfavorable nuclear configuration, since the nuclei are slow moving and do not have time to adjust their positions during the electron jump between the two reactants in a self-exchange reaction, such as

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[†] 2008 marked the Centennial of the American Chemical Society's Division of Physical Chemistry. To celebrate and to highlight the field of physical chemistry from both historical and future perspectives, *The Journal of Physical Chemistry* is publishing a special series of Centennial Feature Articles. These articles are invited contributions from current and former officers and members of the Physical Chemistry Division Executive Committee and from *J. Phys. Chem.* Senior Editors.

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$$\mathrm{Co(NH_3)_6}^{+2} + \mathrm{Co^*(NH_3)_6}^{+3} \rightarrow \mathrm{Co(NH_3)_6}^{+3} + \mathrm{Co^*(NH_3)_6}^{+2} \quad (1)$$

where the asterisk denotes a radioactive tracer isotope. This unfavorability of configuration of the atoms in the newly formed ions meant that the system was suddenly at a much higher energy, and hence the reaction would be slow. The same effect would occur for the solvation coordinates.

When I first read Libby's paper I was enthralled: the Franck–Condon principle designed for spectroscopy was actually applied to the rates of chemical reactions! But then an uneasiness set in. Where was the sudden increase in potential energy coming from? I realized that in this application of the Franck–Condon principle the law of conservation of energy was being violated and that a reorganization of bond lengths and solvent dielectric polarization of the surrounding solvent had to occur both before and after the electron transfer. I focused on the solvation aspect first and followed it with a treatment of this reorganization of the bond lengths.[3]

Self-exchange electron transfers in which no chemical bonds are broken or formed constitute the simplest class of reactions in all of chemistry. A major factor affecting a reaction rate, its standard free energy of reaction ΔG° is missing ($= 0$) in self-exchange reactions, and so the data permitted one to focus on the remaining factors that affect the reaction rate. This simplicity, since no chemical bonds are broken or formed in simple ET reactions, permitted a detailed analysis, leading to an equation for the rate constant

$$k = A \exp[-(\Delta G^\circ + \lambda)^2/4\lambda kT] \quad (2)$$

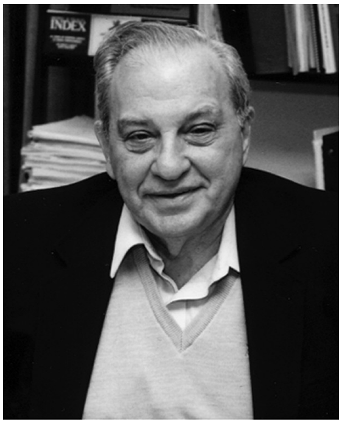
the λ denoting the "reorganization energy", depicted in Figure 1. The intermediate equations in the derivation were very complicated, as can be seen in the original publications, and the simplicity of the final equation came as a major surprise to me, actually a "Eureka" moment.

The many examples of the application of eq 2 to experiments without any numerical calculations include the cross-relation, $k_{12} \cong (k_{11}k_{22}K_{12})^{1/2}$ and the "inverted" effect[3b] believed to play an important role in the high quantum yield of charge separation in photosynthesis.

2. Mass-Independent Fractionation Phenomenon. Typically the fractionation of isotopes in any process is "mass-dependent" and obeys the usual Bigeleisen–Mayer–Urey (BMU) theory[4] of mass-dependent isotope effects. It is obeyed by many systems, as for example for the oxygen isotopes shown in Figure 2.

More recently, unusual isotope effects were observed in the formation of the ozone from O and O_2, both in the laboratory and in the stratosphere, and led to the discovery of mass-independent isotope fractionation "(MIF)".[5] In this phenomenon ^{17}O and ^{18}O were equally enriched in a reaction, in that a plot of the $^{17}O/^{17}O_{Std}$ versus $^{18}O/^{18}O_{Std}$, has a slope of unity instead of 0.52, where Std denotes the isotopic content in a standard sample, ocean water, as in Figure 3. This unusual MIF effect violates the conventional BMU theory and remained a mystery for many years. Ozone is formed in the reactions $O + O_2 \rightleftarrows O_3^*$, $O_3^* + M \rightarrow O_3 + M$, where O_3^* is a vibrationally hot molecule and M is a colliding third body, and the O in the reaction having been formed from O_2 photochemically or by an electric discharge. It occurred to us that MIF might be explained in terms of an incomplete energy randomization (non-RRKM effect) in symmetric ozone molecules, such as $^{16}O^{16}O^{16}O$, $^{16}O^{17}O^{16}O$, or $^{16}O^{18}O^{16}O$, a randomization more incomplete than that in isotopically asymmetric molecules, such as $^{17}O^{16}O^{16}O$ and $^{18}O^{16}O^{16}O$.[6] A small effect, hardly discernible by other experiments (about 15%), would be translated into a slope change in the fractionation plot from 0.52 to unity. The idea served as a basis for an extensive collaboration with my students, Yiqin Gao, Bryan Hathorn, and Wei-Chen Chen.

We assumed that approximate selection rules for the isotopically symmetric molecules restricted the energy redistribution in the vibrationally excited O_3^*, leading to fewer of its vibrational states being coupled to an entrance channel $O + O_2 \rightarrow O_3^*$. In turn, it would lead to a shortened lifetime of the O_3^* and hence to a smaller probability of being deactivated by a



R. A. Marcus, Arthur Amos Noyes Professor of Chemistry at the California Institute of Technology, was born in Montreal, Canada in 1923. After receiving a B.Sc. (1943) and Ph.D. (1946) (experimental research with Carl A. Winkler) from McGill University, followed by post-doctoral research with E. W. R. Steacie at the National Research Council of Canada (experiment) and with Oscar K. Rice at the University of North Carolina (theory), he became a member of the faculty of the Polytechnic Institute of Brooklyn (1951–64) and the University of Illinois (1964–78), and is Noyes Professor at Caltech (1978 to present). His research has been on almost every aspect of chemical reaction rate theory. Among the mainlines are the "Marcus theory" of electron transfer processes and the RRKM (Rice–Ramsperger–Kassel–Marcus) theory of unimolecular reactions. His more recent contributions include semiclassical theory of collisions and bound states, reaction coordinate Hamiltonians, the "mass-independent" isotope effects in stratospheric ozone and other atmospheric molecules, fluorescence intermittency of semiconductor nanoparticles (quantum dots), catalysis of "on water" organic reactions, atom and proton transfer reactions, enzyme catalysis, and single-molecule studies of proteins. A trademark of his research has been a strong interaction between theory and experiment. Marcus received, the Wolf Prize in 1985, the National Medal of Science in 1989, and the Nobel Prize in Chemistry in 1992. He is currently also a Visiting Nanyang Professor at the Nanyang Technological University in Singapore and a Distinguished Affiliated Professor of the Technical University of Munich.

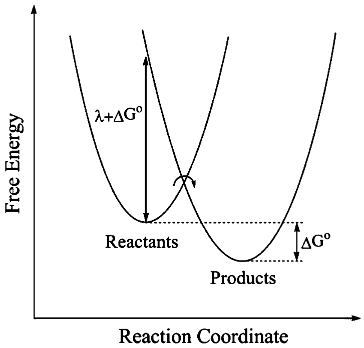


Figure 1. Electron transfer free energy curves. Schematic plot of free energy curves of the electronic states of the QD, the two curves describing the electronic state before and after trapping.[1]

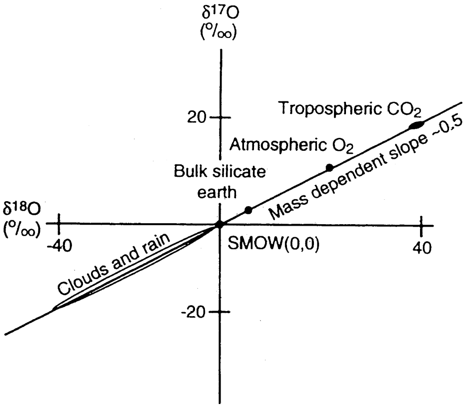


Figure 2. Mass-dependent fractionation for various oxygen containing species.[5b] The origin indicates that the isotopic fractionation is relative to standard mean ocean water (SMOW). (Reprinted from ref 5b with permission.)

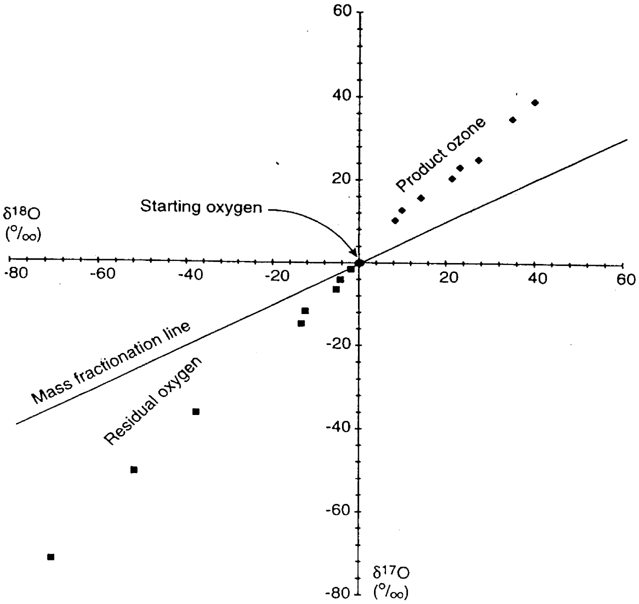


Figure 3. Mass-independent isotope effect in ozone formation.[5c] (Reprinted from ref 5c with permission.)

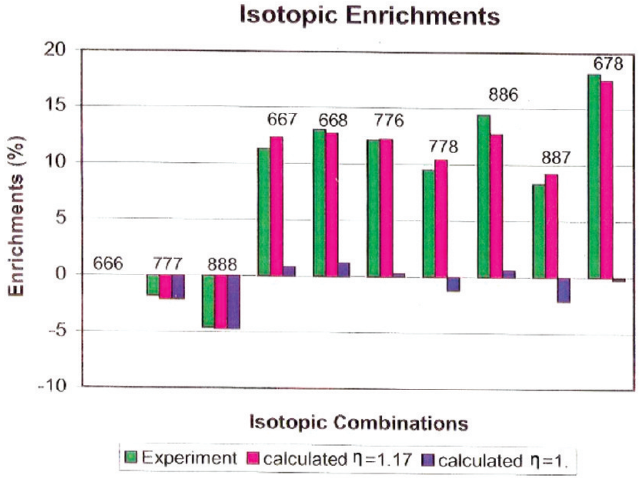


Figure 4. Isotopic enrichments. Mass-independent fractionation for ozone enriched in the heavy isotopes: The small mass-dependent effect is seen in the blue bars. Experiment[5c] and theory.[6b] The η denotes a nonstatistical factor multiplying the density of states ρ for the O_3* molecule: the effective density $\rho_{eff} = \rho/\eta$, where $\eta = 1$ for asymmetric isotopomers, such as 16 16 17 or 18 18 16, and equals some value, 1.17 in this figure, independent of masses, for any symmetric isotopomer, such as 16 16 16 or 16 17 16. (Reprinted from ref 6b with permission.)

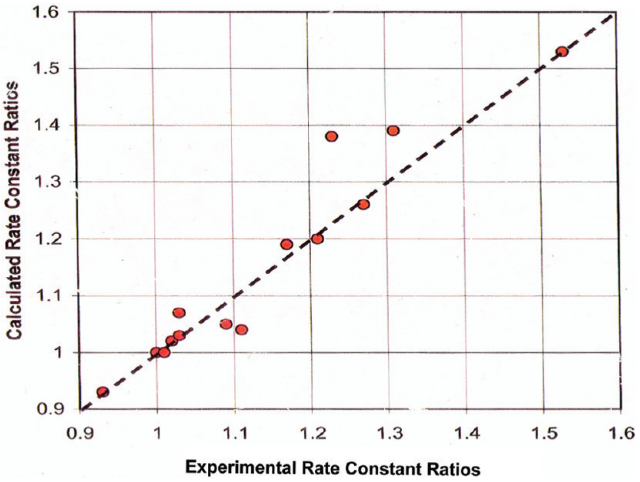


Figure 5. Large mass-independent effect when the ozone recombination experiments are of the "unscrambled type". (ref 6b, using data from ref 5c) The ratio of rate constants is $k_{x+yz}/k_{16+1616}$, where x, y, and z denote oxygen isotopes. (Reprinted from ref 6b with permission.)

subsequent collision of the O_3* with M to form a stable O_3. Since the asymmetric ozone isotopomers were unaffected by the selection rules their lifetimes were less shortened. This symmetry effect would occur equally for ^{17}O and ^{18}O and so lead to a slope of about unity for a three-isotope fractionation plot. Similar remarks apply to the many other isotopomers of ozone. A comparison of theory and experiment for a system heavily enriched in the heavy oxygen isotopes is given in Figure 4.[5c,6b] Conventional mass-dependent effects[4] are seen in this Figure (small vertical bars) but they are small relative to the symmetry effect.

There is a large body of experiments on this MIF, including both pressure and temperature effects. There is also a special mass effect due largely to zero-point energy influences in the two exit channels, XXY → X + XY and XX + Y, in experimentally "unscrambled systems", as in Figure 5.[6] The two kinds of experiments, scrambled and unscrambled, were shown to reveal different aspects of the overall behavior of the ozone recombination reaction.[6]

3. Isotope Effects in Enzyme Catalysis. A different type of isotope effect, principally in H/D/T, has played a prominent role in studies of enzyme catalysis.[7] This field offers challenges not only for computations but also, in the author's view, for qualitative concepts and analytical theory. An example of the kinetic isotope effect for H and D is given in Figure 6 for a particular thermophilic enzyme.[8] It can be seen in the Figure that the kinetic isotope effect, k_H/k_D, for this enzyme is independent of temperature above a certain temperature, the "breakpoint" temperature T_b: above this temperature, the slope of the log k_H and the log k_D plots vs $1/T$ are equal. Below this temperature there is a break in the slopes of the plots. Also, the slopes of the log k_H and log k_D plots are no longer equal and so the ratio k_H/k_D is now temperature-dependent.

This temperature independence of k_H/k_D above T_b occurs for a number of enzymes that are operating on their natural substrate at their natural temperature.[9] It is unlikely that this T-independence can be attributed to an accidental cancellation of opposing factors. Instead, a simple interpretation[10] is that in these enzyme−substrate systems the two reactants are situated naturally at an appropriate separation distance for the H-transfer,

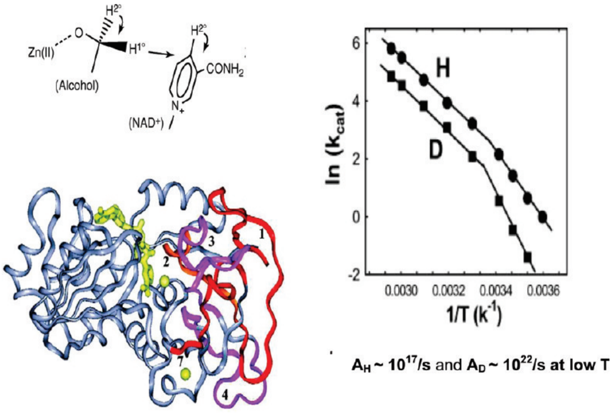


Figure 6. Reaction, structure, and H/D kinetic isotope effect for the oxidation of bensyl alcohol by a thermophobic alcohol dehydrogenase.[8d] (The plots are reprinted from ref 8d with permission.)

so little or no H-stretching is needed to reach the transition state of the reaction. Reaching the TS then involves instead primarily an isotopically insensitive reorganization of the surrounding protein, e.g., reorientation of dipoles and of the H-bonded structure. Further, in this regime where k_H/k_D is T-independent, both the H and the D react (tunnel) from their vibrational ground states.

The break in the slope at T_b in Figure 6 can be viewed in a sense as a phase transformation,[10] a transition somewhat similar to a glass transition, the glass becoming more fluid like above the glass transition temperature T_g. For example, in the latter the activation energy for viscosity is smaller at temperatures above T_g than below T_g. In the case of proteins, flexibility has been emphasized as an important factor in enzyme catalysis.[8c]

As one approach to understanding the change in slope in Figure 6, we suggested[10] an application of Kramers' equation. The latter relates the chemical reaction rate to an effect of an "internal viscosity" in one limit (the overdamped limit) and to a viscosity-independent transition state rate theory in the other (underdamped) limit. It focuses on the behavior in the vicinity of the transition state. Above T_b the Arrhenius pre-exponential factor for k_H calculated from the experimental data in Figure 6 is "normal", namely of the order of $10^{12}-10^{13}$ s^{-1}, and one infers that the protein is quite flexible there. Below T_b the pre-exponential factor for k_H is approximately 10^5 fold higher than it was above T_b. The pre-exponential factor for the viscosity of silica undergoes a similarly large change at the glass transition temperature, a factor of 10^6 or so.[11]

While this simplified approach may prove useful for examining the change in the pre-exponential factor for k_H in Figure 6 it encounters a greater challenge in explaining the much larger change in the pre-exponential factor for k_D. The latter factor is again "normal" above T_b, but below T_b it is of the order of 10^{22} s^{-1}, a result obtained from the data in Figure 6. To explore this large difference in the H and D pre-exponential factors below T_b we recall the extra dimensionality in the reaction. For enzymes the H or D motion is the fast coordinate and in a 2- or a 3-dimensional subspace the protein reorganizational motion X_1 and the separation distance of the two heavy atoms X_2 are the two slow coordinates, and they may be coupled. Descriptions containing more than one coordinate are not uncommon in the enzyme light-particle transfer field. In exploring this approach it is useful to recall early examples of two-dimensional Kramers' type theory.[12] In the present instance, where there may be two instead of one slow coordinate, it would be useful to learn from suitable spectroscopic measurements how much X_1 and X_2 are each slowed down in a system where $T < T_b$. If the distance X_1 before the transition state has to be a smaller for the D than for the H system in order for the D to tunnel effectively in a system where the change of X_1 is important, the extra X_1 motion causes the D rate to be more adversely affected than the H rate by the extra sluggishness of the system below T_b.

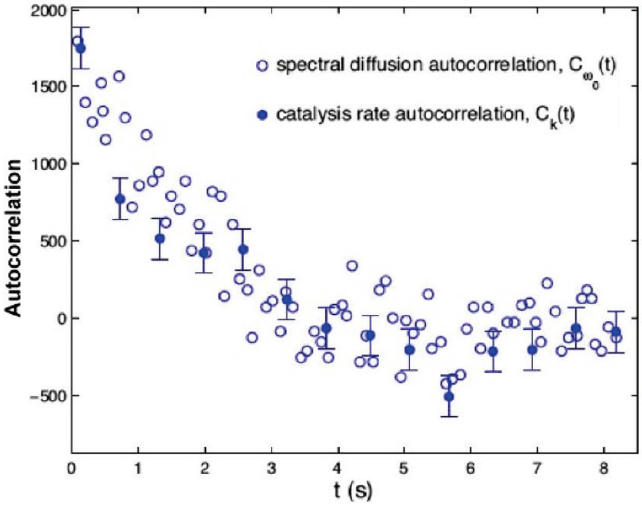


Figure 7. Fluctuations in catalysis rate and spectral diffusion chlorersterol oxidase oxidation of FAD. Comparison of the decay of autocorrelations of catalysis rate fluctuations [$C_{k(t)}$] and spectral diffusion [$C_{\omega_0}(t)$] $C_{k(t)}$ is rescaled to account for the difference in normalization factors for both of these autocorrelations. Data from ref 13, as plotted in ref 17.

Results for the early 2-dimensional treatments cited earlier also lead to the question of whether the reaction for $T < T_b$ for this now more inflexible protein is still "single-exponential" and whether deviations from single exponentiality can be observed in the experiments. The break in the slope of the log k vs $1/T$ plot at T_b and the large pre-exponential factors below T_b are also a challenge to computational studies, since they have not, to my knowledge, been reproduced in computations.

Digression on Single Molecule Studies of Proteins. Correlation Functions for Properties of Enzymes and Other Proteins. The studies in enzyme catalysis have been complemented by single molecule studies of the time-correlation function of fluctuations in catalysis rate.[13−15] Other single molecule properties include those involving spectral diffusion and fluctuations in fluorescence of an excited chromophore in the enzyme. The number of such experimental studies is still limited.

One of these experiments showed a similarity of time scales for spectral diffusion and catalytic rate fluctuations for a particular enzyme, as in Figure 7.[16] A question that Meher Prakash and I addressed recently[16,17] was prompted by this experiment. We asked whether there might be some common denominator to explain it and as a possibility suggested that electrostatic fluctuations at the catalytic site may reflect fluctuations in conformation on a millisecond time scale.[16,17] Electrostatic properties are often invoked in treatments of enzyme catalysis.[18] The fluctuations at the catalytic center can be in orientations of the various dipoles and in positions of charges in the enzyme, and so lead to fluctuations in the local electrostatic field. Making this assumption, we obtained the relation[16]

$$C_k(t) \cong C_{\omega_0}(t) \cong C_{\gamma_r^{-1}}(t) \cong C_E(t) \qquad (3)$$

The $C_k(t)$ denotes a "normalized" time-correlation function of fluctuations in the enzyme catalytic rate constant

$$C_K(t) = \frac{\langle \delta k(t) \delta k(0) \rangle}{\langle \delta k(0) \delta k(0) \rangle} \tag{4}$$

The $C_E(t)$ denotes the time-correlation function for fluctuations in the electrostatic interaction energy at the catalytic site

$$C_E(t) = \frac{\langle \delta E(t) \delta E(0) \rangle}{\langle \delta E(0) \delta E(0) \rangle} \tag{5}$$

while $C_{\omega_0}(t)$ is the time-correlation function for the spectral diffusion, and $C_{\gamma_r^{-1}}$ the correlation function for fluctuations in the fluorescent lifetime of the chromophore at the catalytic site in the absence of fluorescent quenchers.

We had hoped that among the current experimental single molecule studies of fluctuations of enzymes some would permit a test of eq 3. However, instead, no two of the three time-correlation functions have been studied for the same enzyme, apart from the single example that prompted our original study. In the absence of a theory that made predictions there was perhaps little stimulus for making a detailed comparative experimental studies of the different correlation functions for the same enzyme. Future experiments on a single enzyme would permit a test of the relations in eq 3.

There are studies of the correlation function of fluctuations in fluorescent lifetimes of chromophores in proteins where the quenching of the fluorescence is mainly due to electron transfer to some nearby donor or acceptor.[19] Those fluctuations may have a similar or a quite different origin. For example, it has been suggested that they may be due to fluctuations in donor−acceptor separation distance.[19] Because of the millisecond time scale of the correlation functions, they are in any case revealing of conformation changes rather than of simple vibrations, which have considerably shorter correlation times. The purely radiative contribution to the fluctuations in fluorescent lifetimes, $C_{\gamma_r^{-1}}(t)$, in the same enzyme can be studied when any electron transfer quenching agent is removed from the enzyme.

We also noted that[17] the correlation function for the interaction energy $C_E(t)$ can be extracted from dielectric dispersion data for the protein. Using Onsager's regression hypothesis we had[17]

$$\left\langle \frac{\delta E(t) \delta E(0)}{\delta E(0) \delta E(0)} \right\rangle = \frac{E(t) - E(\infty)}{E(0) - E(\infty)} \tag{6}$$

where $E(t)$ is given for a change of dipole in a cavity of radius r_0 by

$$E(t) = \frac{2\Delta\mu^2}{r_0^{\,3}} \mathbf{L}^{-1}\left[-\frac{1}{i\omega} \frac{\varepsilon(\omega) - \varepsilon_c}{2\varepsilon(\omega) + \varepsilon_c} \right] \tag{7}$$

where $\varepsilon(\omega)$ denotes the frequency dependent dielectric dispersion, ε_c is the dielectric constant of the cavity, ε_s is the static dielectric constant of the system outside the cavity, and $\Delta\mu$ the difference in dipole moment of the excited and ground state of the chromophore. $\mathbf{L}^{-1}$ denotes the inverse Laplace transform. It is found that, $C_E(t)$ is given by[17]

$$C_E(t) = \frac{\mathbf{L}^{-1}\left[\frac{1}{i\omega} \frac{\varepsilon(\omega) - \varepsilon_c}{2\varepsilon(\omega) + \varepsilon_c} \right] - \left[\frac{\varepsilon_s - \varepsilon_c}{2\varepsilon_s + \varepsilon_c} \right]}{\left[\frac{\varepsilon_\infty - \varepsilon_c}{2\varepsilon_\infty + \varepsilon_c} \right] - \left[\frac{\varepsilon_s - \varepsilon_c}{2\varepsilon_s + \varepsilon_c} \right]} \tag{8}$$

In eq 8 apart from ε_c there are no adjustable parameters since $\varepsilon(\omega)$ is known. (The factor $\Delta\mu^2/r_0^3$ cancels in deriving eq 8). The ε_c is about 2 if the cavity has only electronic polarization. We had hoped that the dielectric dispersion data would be available for a protein for which at least one of the three time-correlation functions had been measured. However, the available dielectric dispersion data appear thus far only for other proteins.

In the absence of such data we used some parameters in a standard equation for the dielectric dispersion, the Havrilia−Nagami equation,[20] a generalization of the familiar Cole−Cole and Cole−Davidson equations. The results for the lipase catalyzed ester hydrolysis are given in Figure 8. The comparison there would be more meaningful had the dielectric dispersion data had been available for this particular enzyme. An example of the concepts similar to those used to obtain in eq 8 were used earlier to treat the time-dependent Stokes shift (TDSS) of Coumarin 343. The result for water as the solvent is given in Figure 9.[21] It is seen that this TDSS decay plot is multiexponential, due to the variety of relaxation frequencies contributing to the dielectric relaxation of water.

Surface Effects. The Bad and the Good

1. Fluorescence Intermittency of Semiconductor Nanoparticles. The fluorescence blinking of single semiconductor nanoparticles (quantum dots, QD) has been studied extensively in recent years.[22−31] Fluorescence blinking is undesirable for an application of QDs as sensors. This blinking is attributed to a trapping of an electron or a hole from an exciton after an optical excitation. In subsequent excitations there is a radiationless decay of the new exciton, a decay that dominates any fluorescence and arises from an Auger process. Thereby, the QD appears as dark. This idea of Efros and Rosen[22g] is now widely accepted. The trap can either be a surface state of the semiconductor QD, for example, a hole in a dangling surface Se ion in CdSe (hole trapping), or it may exist somewhere outside the quantum dot. In any case, the blinking is an undesirable effect when the QD is used for sensing.

Such single molecule studies have revealed information not obtained in experiments on ensembles, though the two types of experiments are complementary.[24b] Studies of the intermittent fluorescence have uncovered a wide array of interesting phenomena, a power law decay being the most prominent.[23] The fluorescence emission spectrum of the QD depends on the radius of the QD and on its elemental composition. A quantum dot, with numerous attachments used for sensing (but not in the above experiments) is depicted in Figure 10.[23]

An example of a distribution of the "off" (dark) periods of the fluorescence intermittency is given in Figure 11 where it is seen to obey a power law.[23] For the "on" (light) periods it goes over into an exponential-like decay at longer times, as in Figure 12,[23] where results are given for two different incident light intensities. Although the latter curves diverge from each other, we found in these data at 10 K that when the time *t* was scaled by multiplying by the intensity *I*, namely, instead of a plot versus log *t* a plot versus log *It* was used, the two curves coincided.[24b] However, this scaling of the intermittency behavior does not appear to apply at room temperature.[25] Scaling with incident light intensity had previously been used for scaling the spectral

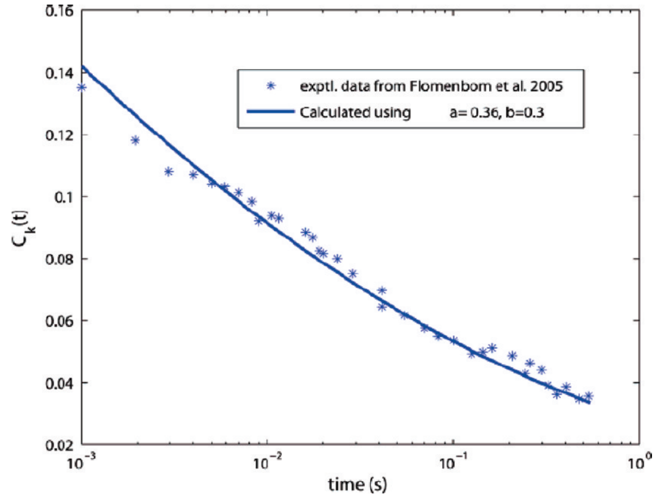


Figure 8. Fluctuations in enzyme catalysis and dielectric. Comparison of $C_k(t)$ of the experiment data of candida Antarctica lipase B with $C_k(t)$ calculated using the dielectric dispersion formula in ref 20.

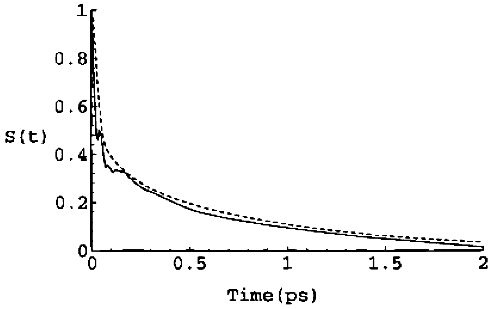


Figure 9. Time-dependent stokes shift of coumarin 343 in water. Calculated $S(t)$ (solid line) for a model of an ellipsoid solute. The ellipsoid has a:b:c = 0.4:1:1 with the dipole moment lying on the b or c axis. The dashed line is the experimental result in ref 44. The theory is given in ref 21. (Reprinted from ref 21 with permission).

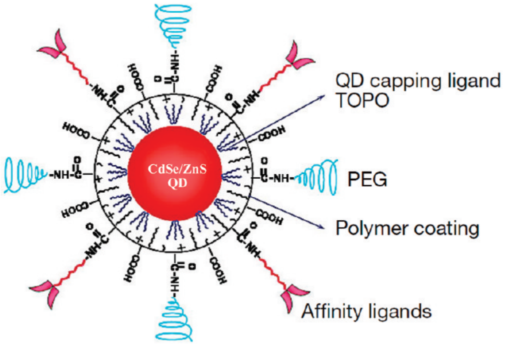


Figure 10. CdSe quantum dot with various attachments for sensing another ZnS coating. Adapted from ref 37. (Reprinted from ref 37 with permission.)

diffusion at 10−40 K.[26] There is no such scalable divergence for the "off" periods, since they do not show any exponential decay.

In treating the intermittency phenomena, we first recall a formalism involving band-edge states near the conduction or valence band, presented in articles with Tang.[24] The pair of electronic states of the system involved in a transition (light to dark, or dark to light) is depicted in Figure 1. A reaction−diffusion equation was set up to treat the intermittency, the diffusion being that of some collective structural coordinate of the QD, the abscissa in Figure 1. When the relevant equations were solved, there were seen to be four time regimes for the intermittency behavior.

In the first of these regimes, a steady-state builds up at the intersection of the two free energy curves in Figure 1. During that time the probability population of the initial state at the intersection begins to approach zero because the interaction with the trap site serves as a sink for that probability. During this period the probability distribution of lifetimes varies as $t^{-1/2}$. In the second of these time regimes, a steady-state at the intersection has been established and the lifetime distribution varies as $t^{-3/2}$. (The probability distribution near the sink behaves as a well-known $(Dt)^{-1/2}$ and the survival probability function is the time-derivative of this function.)

In the next time regime, the effect of a finite slope of the curves at the intersection on the diffusion becomes apparent: it causes a "forced diffusion" that enhances the rate of loss from the intersection region and the survival probability decreases exponentially. In this regime the rate varies as $t^{-3/2}\exp(-\Gamma t)$. (This functional form was later confirmed in experiments.[25]) In the final period, the calculated survival probability distribution of lifetimes is a pure exponential and in this model is due to escape from the bottom of the free energy curve in which it resides.

An example of these results is given in the following equations for an approximate Laplace transform solution to the reaction-diffusion equation for all but the longest times, is given by eq 9[24a]

$$\bar{P}(s) \sim \frac{1}{1+\sqrt{(s+\Gamma)t_c}} \qquad (9)$$

leading to eqs 10a−10c[24a] for the time-dependence

$$\bar{P}(t) \sim \frac{1}{1+\sqrt{\pi t_c}}t^{-1/2} \quad t < < t_c(\text{region 1}) \qquad (10a)$$

$$P(t) \sim \frac{t_c}{4\pi}t^{-3/2} \quad t > t_c(\text{region 2}) \qquad (10b)$$

$$P(t) \sim \frac{t_c}{4\pi}t^{-3/2}\exp(-\Gamma t) \quad t > > t_c(\text{region 3}) \qquad (10c)$$

For still longer times eq 10d was obtained instead of the above equations.

$$P(t) = A\exp(-\gamma t) \quad t \rightarrow \infty(\text{region 4}) \qquad (10d)$$

When the diffusion is anomalous, the −1/2 and −3/2 in these equations become − 1/2 − α and − 3/2 − α, where α is ∼0 to 0.5.[24a]

The critical time t_c depends upon the reaction rate at the intersection of the two free energy curves and on the diffusion constants for motion on the curves. Recently, this prediction of a change in slope of a log $P(t)$ vs log t plot in eqs 10a and 10b was tested experimentally by studying the power spectral density for the distributed lifetimes of the quantum dots.[27] The prediction from eqs 10a and 10b was that there would be a change in the power of the power law at some time t_c. This prediction was recently confirmed in experiments by Pelton et al.[27] The results are reproduced in Figure 13. This confirmation does not mean

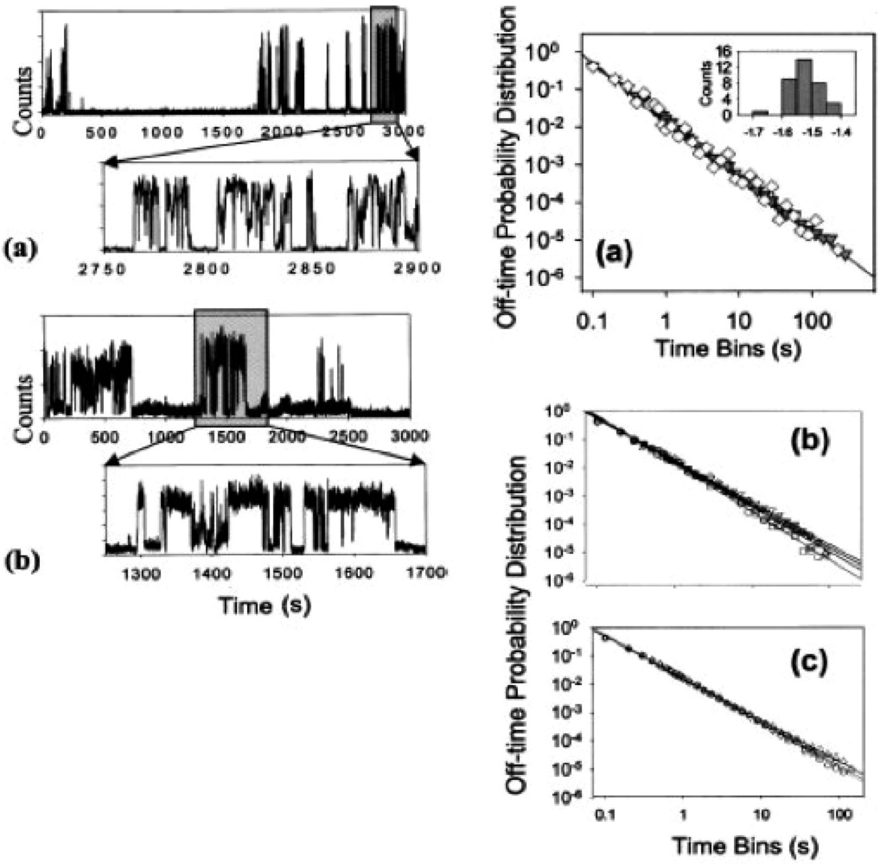


Figure 11. Fluorescence intermittency distribution of “off” times for CdSe(ZnS) QD showing intermittency at (a) room temperature and (b) 10K. Self-similarity is seen in the expanded view.[23] (Reprinted from ref 23 with permission.)

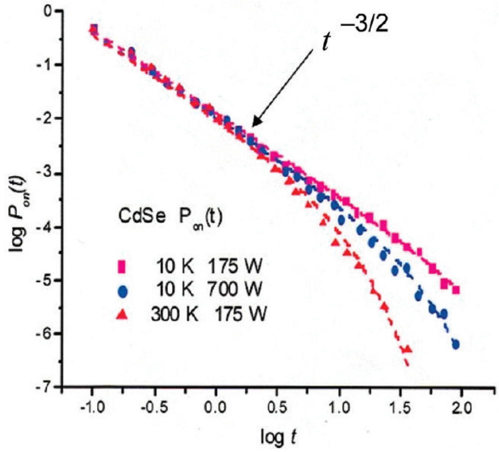


Figure 12. Distribution of lifetimes of “on” state. Average on-time probability distribution for 25-Å radius CdSe(ZnS) QD at 300 K and 175 W/cm^2 (▲), 10 K and 700 W/cm^2 (●), and 10 K and 175 W/cm^2 (■). The straight line is best-fit line with exponent ∼−1.6.[23] (Reprinted from ref 23 with permission.)

that the theory is correct, of course, but it is one hurdle that was crossed.

An important new set of experiments involves different excitation wavelengths at room temperature.[25] The pure power law for the “off” behavior was observed at all excitation energies, but the pure power law for “on” behavior was observed only at low excitation energies. For higher excitation energies, sufficient to optically excite the electron from the valence band (VB) to the 1P$_e$ state, there was an exponential cutoff of the power law, as in Figure 12.

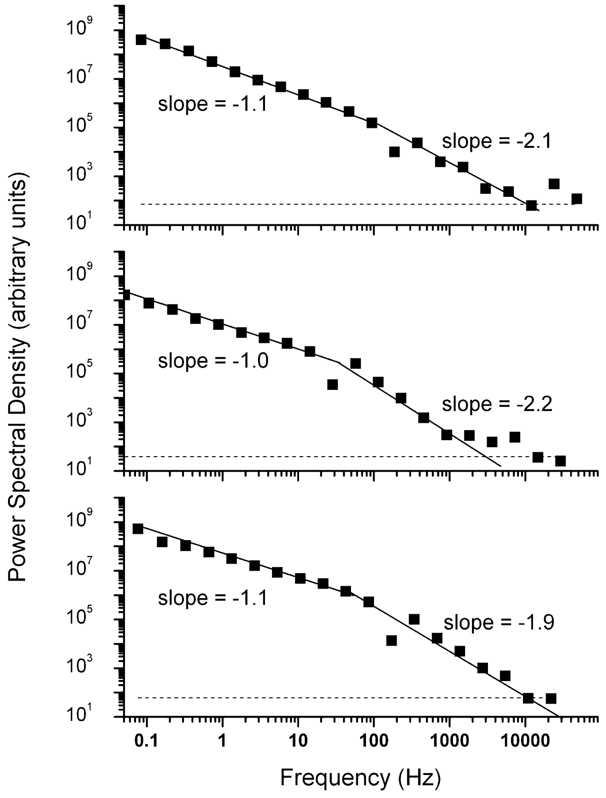


Figure 13. Power spectral density of fluctuations in fluorescence measured for three individual QDs. Solid lines are fitted power laws to low-frequency and high-frequency portions of the power spectra, and horizontal dashed lines are expected shot-noise levels.[27]

The reaction-diffusion model explained a number of the experimental results, such as some tendency for the power in the power law to be ∼− 3/2 on the average, and to there being a cutoff for the "on times". However, it did not explain the asymmetry between "off" and "on" periods and why there is a difference in behavior for lower and higher wavelength excitation. We explore some of these questions next.

In the case of QDs one mechanism (really for "recycling" rather than for trapping) was suggested by Frantsuzov and the author.[28] In this case, the trap is a deep trap near the valence band, a hole trap. (In atomistic terms it could be a dangling Se ion at the surface of the CdSe QD.) The existence of this deep trap is known from an infrared absorption by the QD. This trapping has been monitored by observing the $1S_e \rightarrow 1P_e$ infrared absorption spectrum occurring when a hole is trapped and hence when there is an extra electron in the "conduction band" (CB) $1S_e$ state.[29]

Aside from the distinction between trapping and recycling, the Auger-assisted mechanism in ref 28 is a process in which the excited electron from an electron−hole pair exciton, an electron in the $1S_e$ CB state, goes into the $1P_e$ state, this transition being in resonance with an electron in the "trap" (in our present case a dangling Se^{2-} ion) going into the hole in the valence band created by the excitation. Evidence that the trapped hole is localized rather than distributed over the surface of the QD is seen in the effects of an alternating electric field,[30] where the effect of both enhancement and decrease of the fluorescence can be understood in terms of a trapped charge jumping around (on the surface) rather by a delocalized band.

For concreteness we will suppose that a dangling Se^{2-} ion at the surface of a CdSe QD serves potentially as a trap for an Auger assisted trapping. Upon absorption of light the newly created $1S_e$ electron in the conduction band (CB) could go up to the $1P_e$ state while an electron in Se^{2-} goes down to the newly created hole in the valence band (VB), so forming an $Se^{\bullet -}$ in this Auger-assisted process. For detrapping one possibility is that with the absorption of a second photon, the second $1S_e$ electron in CB goes down to the dangling $Se^{\bullet -}$, converting it to Se^{2-}, while the other $1S_e$ electron goes up to a higher CB electronic state.

In the structural diffusion/reaction formalism postulated in our previous studies, but now adapted to this mechanism, there would be this extra I-dependence due to the absorption of the second photon. However, the kinetics of the "reaction", the conversion of one electronic state of the QD as a whole to another QD state as a whole, trap included, would not be affected by I when in Figure 1 (where the states are now "dressed" by the excitations) the intrinsic reaction rate at the intersection is so fast that the reaction becomes structural diffusion-controlled. At low I the rate of creation of this second exciton becomes small and the reaction at the intersection would no longer be diffusion controlled. The overall detrapping then becomes I-dependent. Indeed, when the incident light is turned off the dark state persists for a relatively long time,[22f] suggesting the importance of a light induced detrapping. The effect of varying I on the lifetime distribution of the dark state at low I does not appear to have been studied experimentally at room temperature for CdSe QDs coated with ZnS.

A very different intensity behavior is found for CdSe QDs coated with CdS, which is much less confining of the exciton in CdSe than QDs coated with ZnS, and so permits an ionization mechanism for formation of the dark state.[22e] This ionization mechanism is very often postulated also for ZnS coated CdSe QDs. A detailed comparison of the effect of I for the two QDs would therefore be of considerable interest. Indeed, since this CdSe/CdS system appears to be one where the electron is ejected outside the QD, it would be useful to see whether it obeys power law kinetics and, if it does, what the power is and whether this QD that is likely to have an ionizing mechanism also shows an exponential cutoff for the "on" state.

At the shorter incident light wavelengths, higher CB electronic states and deeper VB electronic states are excited and other potential Auger mechanisms forming a dark (off) state become accessible. Their nature remains to be explored, but they reduce the probability of long lifetimes of the "on" state, as seen in an exponential cutoff in the log−log plot in Figure 12. A corresponding new high energy process is less likely to occur for the "off" state, since it now has to compete with the very rapid nonradiative decay of the excited electron to the VB, a fast decay that is responsible for the "off" state being nonfluorescent.

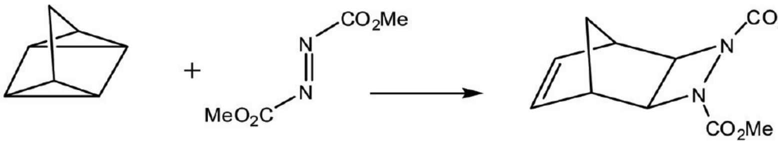
The mechanism just discussed explains several of the experimental observations, such as why the −1.5 power in the power law is a frequent average, rather than the power having quite different value, and in predicting change in the power law at short times. It also explains an asymmetry of the light and dark states at high energies: only for the dark state is there the rapid Auger process that competes very effectively against other processes, such as the one that at the higher excitation energies leads to an exponential cutoff. The mechanism also suggests further specific experiments involving light intensity effects. However, it is not assured that the exponential cutoff found for the 'light' state at high excitation energies is due to a forced diffusion rather than to some other source. Detailed calculations on quantum dots can explore internal consistencies in the assumptions of this or other mechanisms. Such a possibility will be examined elsewhere.

Since this intermittency of fluorescence of the quantum dots is an undesirable feature for their application as sensors efforts have been made to reduce it by modifying the coating of the QD, either in material or in number of layers of the coat as well as varying adsorbed material on the QD.[31] There has been some success in this respect.

2. Surface Chemistry, The Good. Green Chemistry. In a remarkable study, Sharpless and co-workers[32] found that certain organic reactions were greatly catalyzed by shaking the organic reactants with water to form an emulsion. One reaction that normally took 48 h when the two organic reactants alone were mixed, now took ten minutes. This reaction is illustrated in Figure 14 together with a description of the experiment.[33]

Recently, we formulated a theory[34] to treat such reactions, using as a basis results on the nature of the OH group at a water−air and a water−oil surface[35,36] in sum frequency generation (SFG) experiments, These results showed that approximately 25% of the OHs at the surface were "free" instead of being hydrogen bonded; that is, they showed an IR absorption observation based on the peak at ∼3700 cm^{-1}, characteristic of free OHs.

In the on-water catalysis theory formulated by Jung and the writer, the catalysis occurs when the transition state is attracted more to the free OHs than are the reactants. Density functional calculations were made for treating the reacting pairs and the transition state for a small cluster of water molecules. This behavior of the protruding OHs contrasts with the behavior around a small hydrophobic solute. In the latter case, according to neutron diffraction data,[46] the hydrogen bonded structure is intact, as indicated in the schematic sketch in Figure 15, and so there are little or no free OHs there and an OH hydrogen bond



1 **2** **3**

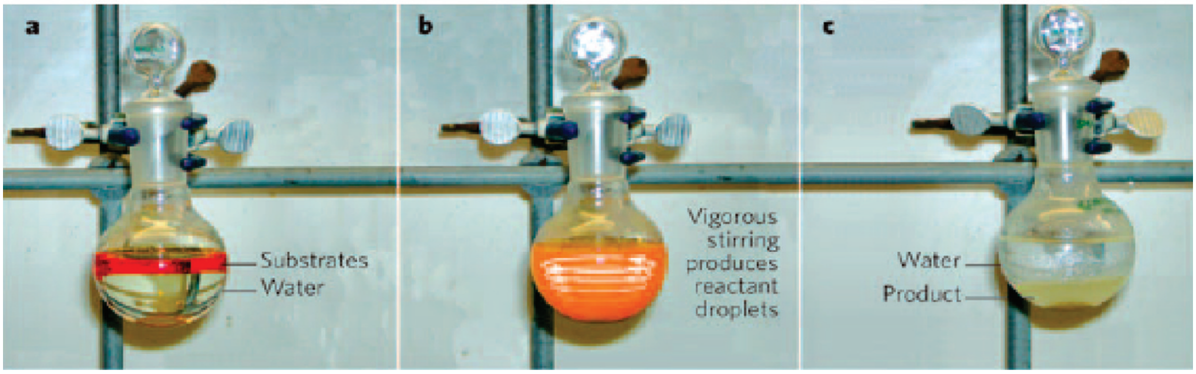


Figure 14. Experimental puzzle: rate acceleration “on water”. Depiction of on-water reaction in a stirred reaction. Adapted from refs 33 and 32. (Reprinted from refs 33 and 32 with permission.)

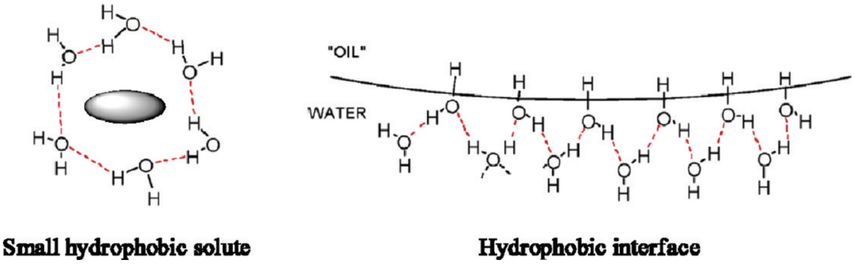


Figure 15. In-water (“molecular surface”) vs on-water (bulk surface). Cartoon of the on-water catalysis in comparison to the organic/ aqueous homogeneous reaction. Sources of experimental data are refs 46 (neutron diffraction) and 35 (sum frequency generation).

or bonds must be broken in order for the water to stabilize the TS. In contrast there are the ca 25% free OHs in the water/air or water/oil interface.[35]

The rate constants of all three experimental arrangements have different units. To compare the reaction rates on a similar basis - in water, on water, and neat (no solvent), it was necessary to introduce some simple statistical mechanical considerations. In this case the reaction times of 48 h for the neat system, 4 h for the homogeneous system, and 10 min for the reaction on water, translated into 2×10^5, 10^3, and 2 s, respectively. Approximate transition state calculations were made for the neat and “on water” reactions and gave results consistent with these values. More detailed calculations are needed and are underway using larger water clusters.

Much remains to be done both experimentally and theoretically. For example, we do not know the size of an emulsion particle in the on water reaction and so assumed some typical value. The reaction order was assumed on physical grounds. For example, for the neat system the molar ratio of the reactants can be varied and it can be seen whether the expected maximum rate occurs at an approximately 1:1 molecular ratio. The experiments thus far have been directed at exploring which reactions were catalyzed by on-water, and with their yields and selectivity.

Crossroads?

In this paper we have given recent examples of studies that involve both analytical and analytical/computational input. These and other examples are in each case experiment-driven. Nature has had adequate time to present many puzzles to the theorist, experimental puzzles that are a rich trove for future theorists. During this past centennial period, and indeed, particularly during the latter half of it, we have seen a major change in theory, particularly in chemistry. Initially, theory was largely analytical, although there were some Herculean efforts at computation as in the 1930s when Joe Hirschfelder cranked out on a calculating machine classical trajectories for a chemical reaction. One can now compute potential energy surfaces and reaction rates far more accurately than at the time around 1950 when I was formulating what later became known as the RRKM theory of unimolecular reactions. In those days, we thought of the transition state (the British term coined by Evans and Polanyi that eventually displaced the American term “activated complex” of Eyring), in terms of “loose” or “tight”, differing in the number of free rotations versus bending vibration in the transition state. Ballpark estimates were made of the preexponential factors of unimolecular dissociations or isomerizations and of bimolecular recombination reactions. Considerably more sophisticated calculations are now available, due to modern computational methods.

Occasionally, the computational results may lead to new concepts or provide evidence for old concepts. An example, I recall from an experience in which I was personally involved,[38] is a result from classical trajectory calculations of Wall and coworkers[39] and quantum calculations of Mortensen and Pitzer[40] for the collinear $H + H_2 \rightarrow H_2 + H$ reaction. In both cases it was found in the computations that increasing the vibrational energy of the H_2 reactant enhanced the probability of reaction. I realized that if one assumed that the vibrational quantum number remained constant during the course of the reaction, or if its semiclassical Bohr-Sommerfeld counterpart, the vibrational action remained constant during the classical trajectories for the reaction, one could explain quantitatively the enhanced reaction probability in both studies, taking tunneling into account in the quantum study.[38,41−43] The nature of this vibration changed enormously during the motion along the reaction coordinate, changing from a vibration of the initial H_2 reactant to a symmetric stretching H_3 vibration of the transition state, and finally to the vibration of the H_2 product. To characterize this behavior of approximately constant the vibrational quantum number or vibrational action, I introduced the term “vibrational adiabaticity”, in analogy with the electronic adiabacity that occurs when systems move on a single electronic surface.[38] Expressions for corrections in the adiabaticity due to changes in frequency and curvature along the reaction path were obtained but this aspect is another topic.[41,42] This concept, first tested by comparison with computer-based results, became a feature of the chemical dynamic literature.

In this article we have discussed simple and complex systems, mainly in the framework of analytical theory aimed at the development of testable equations relating different kinds of measurements. When successful, one may capture the fundamental physics and chemistry in a compact and physically intuitive way that also provides insights into new or related experiments. Examples are given. On the other hand one is aware of the power and relevance of computations. In our own work we could not have addressed the $CO + OH \rightarrow CO_2 + H$ or $N_2O + h\nu \rightarrow N_2 + O$ reactions in the atmosphere or stratosphere in recent studies[45,46] without the detailed computationally obtained potential energy surfaces needed for their study.

As valuable as current computations are, one can raise the question of whether in some cases the study may instead be a matter of data in and data out of the black box, rather than the finding of physical concepts, concepts translatable to other systems. In some cases the analytical approach leads instead to general equations relating theory and experiment, rather than requiring a specific calculation for each system. We all recognize that one of the main goals in research is to capture the physical essence of a phenomenon and use it not only to interpret but also to predict the results of new experiments. One view of theory, demonstrated in the present article, is that experiments are primary, often the source of new theory, and that the interaction of theory and experiment is paramount, each stimulating the other.

Nevertheless, discerning basic theoretical problems in the wealth of available experimental and computational results can be a major hurdle and sometimes the development of the theory can be relatively rapid once the existence of an experimental puzzle is known. The writer continues to be impressed with this exciting interplay of experiment and theory and with many experimental puzzles that exist and that continue to arise in new experiments, when one keeps an eye out for them. For the theoretically oriented students it is perhaps a truism to add that the broader one’s background is in physics, chemistry and mathematics, and the more one is familiar with the new results and the potential and limitations of new techniques, the larger the range of interesting problems that one can address. I for one look forward to the next ACS Centennial, though admittedly this time for all of us from afar.

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