# Fundamentals of Chemistry at Surfaces and Beyond

## Abstract
Fundamental developments in this project include (1) an analytic theory of pooling of infrared quanta on surfaces, with a potential application to laser-selective chemistry, (2) diffusion-electron transfer reaction rate theory for intermittent fluorescence of semiconductor nanoparticles, explaining the power law distribution of bright and dark periods and the exponential tail for bright periods, (3) theory of intermittent fluorescence of dyes on semiconductor nanoparticles and plane surfaces, (4) approximate semiclassical instanton theory for H-tunneling in small and large...
ABSTRACT

Fundamental developments in this project include (1) an analytic theory of pooling of infrared quanta on surfaces, with a potential application to laser-selective chemistry, (2) diffusion-electron transfer reaction rate theory for intermittent fluorescence of semiconductor nanoparticles, explaining the power law distribution of bright and dark periods and the exponential tail for bright periods, (3) theory of intermittent fluorescence of dyes on semiconductor nanoparticles and plane surfaces, (4) approximate semiclassical instanton theory for H-tunneling in small and large systems, computationally less demanding than more accurate approaches and whose utility is being explored, and (5) marked improvement of the range of validity of the maximum likelihood method so as to treat power law data, converging when the common method diverges.

The theory of infrared quanta pooling (accumulation of quanta in individual adsorbed molecules on surfaces) rapid equilibration of the quanta was assumed among the sites and the results were compared with a kinetic Monte Carlo computational solution of the coupled kinetic differential equations. When the assumption is valid (high light intensities), the theory has applications to infrared laser selective chemistry on surfaces. Research has also been initiated on a fundamental electron transfer theory for perovskite-like and other photovoltaic solar cells.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<table>
<thead>
<tr>
<th>Received</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>03/21/2012</td>
<td>4.00 Rudolph A. Marcus. At the Birth of Modern Semiclassical Theory,</td>
</tr>
<tr>
<td></td>
<td>Molecular Physics, (03 2012): 0. doi:</td>
</tr>
<tr>
<td>07/28/2011</td>
<td>2.00 Nathan O. Hodas, Yousung Jung, Yanting Wang, R. A. Marcus. Microscopic structure and dynamics of air/water interface by computer simulations—comparison with sum-frequency generation experiments, Physical Chemistry Chemical Physics, (02 2011): 0. doi: 10.1039/c0cp02745f</td>
</tr>
<tr>
<td>08/04/2011</td>
<td>3.00 Maksym Kryvohuz. Semiclassical instanton approach to calculation of reaction rate constants in multidimensional chemical systems, Journal of Chemical Physics, (03 2011): 0. doi:</td>
</tr>
<tr>
<td>09/17/2013</td>
<td>13.00 . Theory of Vibrational Equilibria and Pooling at Solid-Diatom Interfaces, J Chem Phys, (09 2013): 0. doi:</td>
</tr>
</tbody>
</table>

**TOTAL:** 7
(b) Papers published in non-peer-reviewed journals (N/A for none)

<table>
<thead>
<tr>
<th>Received</th>
<th>Paper</th>
</tr>
</thead>
</table>

**TOTAL:** 2

(c) Presentations

Lecture: Electron Transfers and Other Reactions in Chemistry, Baku State University, Azerbaijan, 2012
Lecture: From Experiment to Theory to Experiments - Electron Transfer Reactions in Chemistry, Tumkur University, Tumkur, India, 2012
Lecture: Electron Transfer Reactions, H Transfers in Enzymes, and "On-Water" Reactions, National Centre for Biological Sciences, Bangalore, India, 2012
Lecture: Electron Transfer Reactions, H Transfers in Enzymes, and "On-Water" Reactions, University of Hyderabad, Hyderabad, India, 2012

**Number of Presentations:** 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<table>
<thead>
<tr>
<th>Received</th>
<th>Paper</th>
</tr>
</thead>
</table>

**TOTAL:**
Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<table>
<thead>
<tr>
<th>Received</th>
<th>Paper</th>
</tr>
</thead>
</table>

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

<table>
<thead>
<tr>
<th>Received</th>
<th>Paper</th>
</tr>
</thead>
</table>

09/17/2013  
14.00  

TOTAL: 1

Number of Manuscripts:

Books

<table>
<thead>
<tr>
<th>Received</th>
<th>Paper</th>
</tr>
</thead>
</table>

TOTAL:

Patents Submitted

Patents Awarded

Awards
Honorary Doctor of Science, Tumkur University, India, 2012
Honorary Doctor of Science, University of Hyderabad, India, 2012
Postage Stamp, Ghana, 2013
The Prof. Rudolph A. Marcus Award, Journal of Spectroscopy and Dynamics, 2013
Conference in Honour of the 90th Birthday of Rudolph Marcus, Nanyang Technological University, Singapore, 2013
Honorary Doctor of Laws, University of Calgary, Canada 2013
John G. Kirkwood and Arthur A. Noyes Professor of Chemistry, California Institute of Technology

<table>
<thead>
<tr>
<th>Graduate Students</th>
<th>NAME</th>
<th>PERCENT_SUPPORTED</th>
<th>Discipline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Evans Boney</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Yun-Hua Hong</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FTE Equivalent:</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total Number:</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Names of Post Doctorates</th>
<th>NAME</th>
<th>PERCENT_SUPPORTED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wei-Chen Chen</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Sandor Volkan-Kacso</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Zhaoyan Zhu</td>
<td>0.72</td>
</tr>
<tr>
<td>FTE Equivalent:</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Total Number:</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Names of Faculty Supported</th>
<th>NAME</th>
<th>PERCENT_SUPPORTED</th>
<th>National Academy Member</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rudolph A. Marcus (PI)</td>
<td>0.12</td>
<td>Yes</td>
</tr>
<tr>
<td>FTE Equivalent:</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Number:</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Names of Under Graduate students supported</th>
<th>NAME</th>
<th>PERCENT_SUPPORTED</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTE Equivalent:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Number:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Student Metrics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Student Metrics</td>
<td>This section only applies to graduating undergraduates supported by this agreement in this reporting period</td>
</tr>
<tr>
<td>The number of undergraduates funded by this agreement who graduated during this period:</td>
<td>0.00</td>
</tr>
<tr>
<td>The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:</td>
<td>0.00</td>
</tr>
<tr>
<td>The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:</td>
<td>0.00</td>
</tr>
<tr>
<td>Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):</td>
<td>0.00</td>
</tr>
<tr>
<td>Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:</td>
<td>0.00</td>
</tr>
<tr>
<td>The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense:</td>
<td>0.00</td>
</tr>
<tr>
<td>The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Names of Personnel receiving masters degrees

Names of personnel receiving PHDs

Names of other research staff

<table>
<thead>
<tr>
<th>NAME</th>
<th>PERCENT_SUPPORTED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maksym Kryvohuz</td>
<td>0.10</td>
</tr>
</tbody>
</table>

FTE Equivalent: 0.10
Total Number: 1

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachments. Incidentally, two publications listed in an earlier report as being non peer-reviewed were reviewed.
Technology Transfer
## Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Statement of the Problem</td>
<td>1</td>
</tr>
<tr>
<td>2. The Most Important Results</td>
<td>1</td>
</tr>
<tr>
<td>3. Fundamentals of Surface Chemistry and Beyond</td>
<td>2</td>
</tr>
<tr>
<td>4. Bibliography</td>
<td>6</td>
</tr>
</tbody>
</table>

## Statement of the Problem

This research is aimed at understanding fundamental processes such as accumulation of vibrational quanta in molecules adsorbed on surfaces, with a view to application to infrared laser selective chemistry, and understanding the behavior of other surface-focused systems ranging from electron transfer in semiconductor nanoparticles, as revealed in their intermittent fluorescence, to phenomena related to photovoltaic solar cells and catalysis of chemical reactions at liquid interfaces involving water. Analytic theory, and its interaction with experiment and computations plays a key role in this research. The current findings of the research performed with this grant support are summarized and publications are included.

## The Most Important Results

- An analytic theory was given for vibrational pooling of molecules on solid surfaces. The theory has application to infrared laser selective chemistry on surfaces, for example, to the recent strange history of such chemistry on a hydrogen-terminated silicon surface, a passivated surface important because of its enhanced stability in ambient environments. SECTION A.1

- A diffusion controlled electron transfer theory was given for the intermittent fluorescence of semiconductor nanoparticles that incorporates for the first time the main quantitative features of the phenomenon: a power law for the distribution of light and dark periods that is usually centered on -1.5 complemented by an explanation of why only dark periods have a “simple” power law but the light periods have a power law plus an exponential tail. The extensive studies of the optical properties of semiconductor nanoparticles in the literature is prompted by their use in biological sensing, photovoltaic devices, electro-chemiluminescent displays, and solid state lighting. SECTION B.1

- A theory for the intermittent fluorescence of dye molecules on semiconductor surfaces was developed that is based on diffusion controlled electron transfer. This theory accounts for the -1.0 power law for the distribution of dark states after photoinjection of electrons from the excited dye molecules into a semiconductor. The theory provides also an answer to the question why the same behavior can occur also for the light periods. Then, electron transfer is from excited dye molecules to defect surface states located within the band gap of the semiconductor...
instead of electron injection into its conduction band. This concept is new and
covers hitherto unexplained observations in the field of organic/inorganic solar
photovoltaics. SECTION B.2

- We developed the methodology in the maximum likelihood theoretical treatment,
of power law data for surfaces. In particular we devised a maximum likelihood
method that, unlike a conventional method in the literature, has no singularity. We
applied the result to single molecule experiments for photo injection of electrons
from dyes into surfaces. SECTION B.3

- A semiclassical instanton method for studying kinetic isotope effects in reactions
was simplified, a subsequent development being the use of potential energy surfaces
“on the fly”. SECTION C

Several works of this project show the power of analytic treatments, in their own right,
and in their interaction with computations and with experiments.

**Fundamentals of Chemistry at Surfaces and Beyond**

A. Infrared Laser Selective Chemistry

A1. Analytic Theory for Infrared Pooling and Tests of Theory

This research is aimed at understanding fundamental processes such as accumulation of
vibrational quanta in molecules adsorbed on surfaces, with a view to application to infrared laser
selective chemistry, and understanding the behavior of other surface-focused systems ranging
from electron transfer in semiconductor nanoparticles, as revealed in their intermittent
fluorescence, to phenomena related to photovoltaic solar cells and catalysis of chemical reactions
at liquid interfaces involving water. Analytic theory, and its interaction with experiment and
computations plays a key role in this research. The current findings of the research performed
with this grant support are summarized and publications are included.

The question of infrared laser selective chemistry has been and still is a subject of much interest.
During the course of this research we have developed an analytic theory of pooling of infrared
quanta of an adsorbate on a surface\(^1\) permitting an understanding of the experimental data and
the results of our and others’ numerical computations. In the theory one obtains the population of
vibrational states of the adsorbate molecules. To this end we used statistical mechanics, letting
the system equilibrate among the vibrational states of the adsorbate at each time \(t\). This
assumption of vibrational equilibration amounted to assuming that pooling (accumulation of
quanta on individual adsorption sites) and depooling are fast relative to all other processes, such
as loss of quanta to the solid. We also assumed that only one-quantum exchanges occur between
adsorbed molecules and that the energy transfer between the adsorbate and the solid is limited in
pooling by the physics-based assumption of not having a transfer of a quantum larger than the
vibrational quantum corresponding to the Debye frequency cut-off of the solid. The latter
provides a key difference from pooling\(^2\) in the gas phase.

We then calculated and minimized the free energy of the adsorbate, subject to these constraints.
We obtained the distribution of vibrational states of the adsorbate, an inverted distribution rather
than a Boltzmann distribution, and tested the theory by comparing this statistical result with our numerical solution of the “master equation”. The latter is a set of many coupled kinetic ordinary differential equations for the vibrational population of the different sites on the surface, describing the many processes that occur between the quantum states of the adsorbate molecules, between these quantum states and the solid, and for the loss of energy by fluorescence of the adsorbed molecules.

The numerical solution of these coupled differential equations was obtained using a kinetic Monte Carlo integration, using an earlier procedure in the literature. We then compared the numerical results with the existing experimental data and with our analytic theory. An ultimate goal is to combine this theory for pooling with a theory for chemical reactions on the surface, and use the overall theory to predict when infrared laser selective chemistry for adsorbates on solids can occur and when it cannot. A second goal was to explain why the kinetic results were a single exponential decay, even though there are numerous first and second order kinetic processes occurring. The answer, we showed, is a rapid equilibration among the vibrational states of the adsorbed molecules. There have been recent uncertain experiments on laser selective chemistry in this field, and a goal of the theory is to point to conditions for new experiments that can explore this issue. This work is ongoing. The first paper in this series will appear in an October issue of the Journal of Chemical Physics.

A2. Infrared Laser Selective Desorption of H₂ from an Si-H Surface

In the context of infrared laser selective chemistry a Science paper appeared on infrared laser-selective desorption of H₂ from an Si-H surface in the presence of excess Si-D. Since the experimental results could not be reproduced for technical reasons, we focused on other spectroscopic data on the Si-H surface, and with our analytic theory, complemented by a kinetic Monte Carlo solution of the differential equations, and the using other SiH data we are investigating the problem anew and obtained conditions for sufficient pooling as to yield the infrared dissociation of the H₂ using an intense laser. The pooling greatly increases with high light intensity. We are preparing a paper analyzing these results and those of Sum Frequency Generation (SFG) experiments on an Si-H surface.

B. Intermittent Fluorescence in Single Particle Studies

B1. Theory of Power Law and Exponential Tail for Intermittently Fluorescing Semiconductor Nanoparticles

This area has been the subject of numerous experimental and theoretical studies for the past two decades, e.g., 11-19. In our current work we have set up a unified theory that explains some facts for which there was no previous quantitative unified treatment, including our own earlier work, e.g., 15, 20-27. Rather they described various aspects of the problem but not as whole. Key facts are that both the light and the dark periods (fluorescing and non-fluorescing periods) show a power law with a slope averaging about -1.5 for a plot of the log of the “waiting time” distribution versus the log of the time, for both the dark and the light periods, while only the bright period has an exponential tail in this plot, and the onset of the tail varies as the square of the light intensity.

In the present work we again set up a reaction-diffusion differential equation for the “structural diffusion” in the nanoparticle (“spectral diffusion”), including now both excitons and
biexcitons$^{28-32}$, to explain these and other experimental facts. In this way, we developed a theory in which the -1.5 power law aspect arises from a slow structural diffusion of the system which permits it when the initial and final states are “in resonance” (same energy), to go from light to dark or dark to light states. The exponential tail is explained in terms of the biexciton, a high energy system that doesn’t require a resonance to occur due to the formation of biexcitons. The theory also provides an explanation of why the exponential tail does not occur for the dark state.

A number of other experimental facts, such as the dependence of the tail on the square of the light intensity are also explained and predictions made. We obtained a numerical solution of the problem, but an expansion at long times provides simple and valid expressions to compare with the experimental data, such as the -1.5 power law and the exponential tail that varies as the square of the light intensity. The theory is described in a paper being prepared for publication.

B2. Theory of Intermittent Fluorescence of Single Molecules on Plane Surfaces and on Sintered Nanoparticles

In single molecule studies of injection of an electron from a photoexcited dye into a semiconductor crystal or into a film of sintered semiconductor nanoparticles$^{30,31}$, a power law was observed for the distribution of dark periods (dye cation periods in the case studied) for the return of the electron to the dye. When the injection is into a semiconductor with a wide band gap, the distribution of injection times also follows a power law with a slope of -1 in the rare examples studied. In this case the injection is into a trap.

In this work we set up and solved the partial differential equations describing this system (Laplace transform) and also obtained the approximate (long) times appropriate to cover the experimental observations$^{32}$. With this solution it provided the answer as to when a power law for the waiting time distribution may be expected and what that power might be. When the injection is into the conduction band we obtain a power law only for the return of the electron to the dye cation but not for the injection. After a short time the log-log waiting time distribution for the return of the electron to the dye cation has a slope of -1. When the injection is into the band gap a -1 power law is predicted for both the injection and the return.

The data$^{30,31}$ were discussed in terms of theory. A corollary was that single molecule studies for the injection can determine whether the injection is into the band gap or into the conduction band. The theory was applied to single molecule studies of systems, such as dye-TiO$_2$, dye-Al$_2$O$_3$, and dye-ZrO$_2$ systems, and to dye hole injection$^{33}$ into a p-type NiO semiconductor. An article on these results was published in *J. Phys. Chem. C.*$^{32}$

B3. A Maximum Likelihood Method for Power Law Distribution that Does Not Break Down When the Slope is Close to Unity

We formulated a general maximum likelihood estimation (MLE) method for analyzing experimental data with a power law form, with any power exponent, which does not break down for a power close to -1$^{34}$. It contrasts thereby with a standard literature procedure$^{31,35,36}$ that does break down for this particular important power (it has a singularity there). Our method, which uses a sum instead of an integral, can be extended to a power law with an exponential tail and more generally to other distributions. Inasmuch as the theoretical value of the power for dye
sensitized charge recombination on surfaces of semiconductor systems, and for certain charge
injection, is -1 (topic B2), the present correction to the current MLE method has immediate
application to the data in these systems. The results of this research were published in *J. Phys.
Chem. C*.  

**B4. Fundamental Theory of Organic/Inorganic Hybrid Solar Cells**

In the field of solar cells we are developing equations that take account of trap states and that
does not assume an equilibration of the population in those states. We have set up differential
equations for photo-excitation, electron injection, migration, recombination, and electron transfer
at electrodes, simplifying the problem by assuming that diffusion is fast (so converting a partial
differential equation into an ordinary one). To explain an experimental observation of a
“stretched exponential” recovery time in some experiments 37, instead of a simple first or second
order recovery, we do not use a common assumption that the population in the traps is
equilibrated. In this research there has been a synergy with the kinetic concepts we use here and
those for equilibration that we used in the pooling study. This work is an ongoing project and
will treat the older, e.g., 38-43 and newer (perovskite-like) solar cells, e.g., 44, 45. The theory will be
compared with theories that assume equilibration. The P.I. contributed to a chapter of J.A.
Bisquert on the theory of photovoltaic solar cells.  

**B5. Sum Frequency Generation Study of Water-Air Surface**

We studied a model that we used 47 for catalysis 48 of an organic (cyclo addition) reaction in a
water-organic emulsion catalysis by a free (not hydrogen bonded) OH group of a water molecule
at the interface) by studying experiments based 49, 50 on Sum Frequency Generation, a surface
sensitive technique. Different polarizations of the visible and infrared lasers, the infrared tuned to
an absorption at 3700 cm⁻¹, the peak specific for a surface water molecule that has a free non
hydrogen bonded OH group. We studied various polarizations of the SFG experiments, and
calculated SFG signal intensities for each. We used the integrated intensity of the absorption
peak and compared the molecular dynamics/statistical results for the observed second under
susceptibility coefficient. In contrast to most other SFG theoretical studies, e.g., 51-54 absolute
intensities were calculated, using transition dipole moments and polarizability matrix elements
obtained from non-SFG experiments.  

**C. Beyond Surface Studies**

**Semiclassical Evaluation of Kinetic Isotope Effects in a 13-Atom System**

The semiclassical instanton approach was discussed by Dr. Maksym Kryvohuz 56, a member of
the group, and applied to calculate the kinetic H/D isotope effect (KIE) of intramolecular
hydrogen transfer in cis-1,3-pentadiene in a paper published in *J Chem Phys*. 57 All 33 vibrational
degrees of freedom were treated quantum mechanically with a semiclassical approximation.

Nuclear quantum effects such as tunneling under the barrier and zero-point energy were
automatically incorporated in the theory, and were shown to be responsible for the observed KIE
in cis-1,3-pentadiene. The numerical calculations were performed using an empirical valence
bond potential energy surface and compared with the previous experimental and theoretical
studies. An estimate of heavy-atom ¹²C/¹³C KIE in the same system was also provided and the
factors contributing to it were discussed. The method is an approximation to a more rigorous
instanton method 58 with less computation needed. Its utility is being explored by Kryvohuz (now
at Argonne) in an application to enzyme catalysis. After leaving the group Kryvohuz further extended the utility of the theory by introducing on-the-fly high level electronic structure potential energy computations for the chemical reactions.⁵⁹

Bibliography


9


Bibliography