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# RPPR Final Report
as of 26-Oct-2022

Agency Code: 21XD

Proposal Number: 71626CH **Agreement Number: W911NF-18-1-0070**

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**Report Date:** 14-Apr-2022 Date Received: 05-Aug-2022
**Final Report** for Period Beginning 15-Jan-2018 and Ending 14-Jan-2022
**Title:** Novel Surface Phenomena
**Begin Performance Period:** 15-Jan-2018 **End Performance Period:** 14-Jan-2022
**Report Term:** 0-Other
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**STEM Degrees:** 2 **STEM Participants:** 2

**Major Goals:** 1. Sum Frequency Generation (SFG) Spectroscopy.
The major goal in this project is to study dangling OH bonds at a water interface by comparing theory and experiment for SFG, a surface sensitive spectroscopy method. In this work we developed a method to calculate absolute intensities in SFG, to make a more quantitative comparison with the experimental data, rather than calculating only the conventional relative SFG intensities in the spectrum. It will be recalled that SFG involves both an infrared laser and a visible laser as input and the combined outgoing signal as output and that as a consequence of this “nonlinearity” (response to the product of two signals) this response has zero signal in a centrosymmetric system, such as the interior of a liquid. It is thereby a highly sensitive technique for studying the composition of interfaces, in the present case a water-air interface. In SFG experiments the infrared and a visible laser are used to illuminate an interface at a glancing angle and the intensity of the combined outgoing beam is measured. Different polarization combinations of the three beams are studied. We studied the dangling OH groups at a water surface, groups that are believed to be involved in catalysis of organic reactions at surfaces in water-organic emulsions. The dangling 0H gives rise to a narrow peak in the spectrum around 3750 cm(-1). The immediate goal was to see if, using polarizability and infrared and Raman spectroscopic data on OH groups in H20 vapor (where there are no hydrogen bonds)) we could use molecular dynamics trajectories to predict the absolute values of the frequency-dependent SFG susceptibility for the dangling 0H groups. Previously, relative intensities had been extensively studied theoretically and compared with experiment.

2. Biological Rotary Nanomotor ATPase Theory.
In this work the goal was to understand in more detail the sequence of events in single molecule experiments on a biological nanomotor, F1 ATPase, involving in the hydrolysis direction the entrance of ATP (adenosine triphosphate) into a cleft between protein subunits in the nanomotor, its subsequent hydrolysis to form ADP (adenosine diphosphate) and subsequent product release from the cleft and how these processes are coupled, to the rotation of the motor so permitting the motor to interconvert mechanical and chemical energy. More specifically we used data on fluorescence on-off distributions, using a nucleotide (an ATP or ADP) that is modified to include an attached fluorescent moiety. It fluoresces when the ATP or ADP is bound in the cleft and is nonfluorescent when it is in the surrounding solution. A specific goal was to find evidence for a previously undetected but postulated reaction intermediate step and determine properties, such as the lifetime of the intermediate and the rotation angle where it occurs. We explored this problem for the two different species of the F1-ATPase for which experimental data were available, one for a thermophilic protein (operates at high temperatures) and another for a mesophilic protein (operates at moderate temperatures).

3. Electrical Conductivity of Molecular Junctions.

Theories in this field have described “off resonance” conductance (Landauer theory) in which the Fermi levels of the two metallic leads are far removed from a quantized energy level of the conductive material in the junction and “near resonance” theory (Marcus electron transfer theory) in which these two leads have Fermi levels that are close to a quantized energy level of the molecular junction. Recently a unified theory that combines the two in a consistent manner has been proposed in the literature (and has been extended to treat thermal conductivity of molecular junctions). This unified theory was based on the use of a “spin-boson” Hamiltonian, a theory widely used in solid state physics but also a theory that neglects any solvation entropy effects. These entropy changes can be significant when the electron transfer reaction at either metallic lead to the conducting molecule is a charge recombination or a charge creation (and minor when the reactions are of the charge shift type). Our goal is to add to the theory of these conductive molecular junctions, by including the missing solvation entropic effects and still bridge the gap between Landauer and Marcus theories.

4. Drude-Smith Electrical Conductivity Equation.
The Drude-Smith theory is widely used to treat the frequency-dependent electrical conductivity of disordered and somewhat disordered materials in the disorder regime. One of its merits is that it contains only two adjustable parameters, unlike most other approaches. A defect, as Smith himself noted, and has been widely commented on in the literature, is that in the Drude-Smith theory it is assumed that a charged particle that moves in the field due to the other charges undergoes only a single scattering event, whereas there may be multiple scattering events.

5. Electron-Phonon Interactions in Lead Halide Perovskites.
Lead halide perovskite semiconductors have low-frequency phonon modes within the lead halide sublattice. Electron-phonon coupling governs hot-carrier relaxation, carrier mobilities, carrier lifetimes, among other important electronic characteristics. The key idea was to use terahertz spectroscopy to directly observe the interplay between free charge carriers and phonons with the goal of obtaining details on how phonons impact these properties (e.g., exciton populations and other collective modes). A goal is to observe the delicate interplay among charged carriers, phonons, and excitons in mixed-cation and mixed-halide perovskite films by simultaneously resolving the contribution of charge carriers and of phonons using time-resolved terahertz photoconductivity spectra.

6. Contribution to a Collection of Articles in The Journal of Chemical Physics Celebrating the 65th Anniversary of the PI’s Nobel Prize 1956 Article on the Theory of Electron Transfer Reactions.
The goal was to contribute a brief historical article on the electron transfer theory that was recognized by the 1992 Nobel Prize in Chemistry. The article describes the origins of the theory, a theory prompted by the suggestion by Bill Libby that the Franck Condon principle is involved in understanding electron transfer rates and how the experimental data prompted the formulation of the theory.

**Accomplishments:** 1. Sum Frequency Generation (SFG) Spectroscopy.
We explored the statistical mechanical/quantum mechanical theory for the SFG spectrum of dangling (i.e., not hydrogen bonded) OH bonds at a water-air interface. An aim, as noted earlier, was to test an SFG theory by comparing computed and observed absolute SFG intensities, using no adjustable parameters. We first identified which OH’s in the system are at the water surface, and so are dangling OH’s. To do so we used a plot of Auer and Skinner of local OH bond frequency versus the local statistically averaged electric field. The latter plot had been obtained from quantum mechanical studies of water clusters. The OH’s that are in the bulk of the water would be, when averaged over a statistical ensemble, in a zero local electric field. We used molecular dynamics and statistical mechanics to determine the average local electric field at each of the OH’s near the surface. And then used the Auer-Skinner plot to obtain the spectrum for the 3750 cm (-1) band. The SFG susceptibility can be expressed in terms of a time-correlation function involving the transition dipole moment and the polarizability matrix element of the dangling OH’s. To complete the calculation of the absolute (rather than only relative) SFG susceptibility versus frequency we needed these matrix elements and used infrared and Raman measurements of water vapor, since the OH’s in the latter are not hydrogen bonded. Typically, theoretical work on this SFG does not include the dynamical effect of motional narrowing of this 0H band, so making difficult a direct comparison of theory and experiment. To bypass this problem in this test of the theory we made use of a spectroscopic sum rule which permit a comparison of the integrated spectrum of the OH bond and is independent of dynamical effects, such as motional narrowing. The results were successful: theory and experiment agreed within a factor of 1.3 for the single term polarization combinations (“SSP” and “SPS”) with no adjustable parameters. (The polarization combination PPP has four terms that have different partially cancelling signs and is small and, as expected, agreed less well.) Considering the many aspects of the calculation we find this agreement between theory and experiment to be striking. The results were published in Proc. Nat. Acad. Sci.

2. Biological Rotary Nanomotor ATPase Theory.

We developed a method to extract missing states in F1-ATPase rotation experiments. In the F1-ATPase, Thermophilic Bacillus (ThF1) we treated available data and uncovered evidence for an intermediate in the hydrolysis kinetic cycle in which all (three) beta subunits of the F1-ATPase were occupied by nucleotides (ADP and ATP) and that has a short lifetime, ~10 μs. It was previously undetected in the kinetics experiments but was postulated from crystallographic studies. Recently, we extended the method to study a similar phenomenon for a quite different F1-ATPase of the Paracoccus Denitrificans species (PdF1), one that has 120° steps instead of two, 80° and 40° steps. In our previous analysis of the ThF1, using an established sequence of 3 specific states, a theoretical profile of angular jumps is predicted in a plot of a discretized angular velocity versus rotation angle, that agrees with experiment for most of the angular range. Agreement was achieved at all angles by assuming a fourth state with an ～10 μs lifetime and a dwell angle about 40◦ after the ATP binding dwell. The latter result suggests that the ATP binding in one β subunit and the ADP release from another β subunit occur via a transient whose lifetime is ～10 μs and this lifetime is about 6 orders of magnitude smaller than the lifetime for ADP release from a singly occupied F1-ATPase. For the recent work on PdF1, a two-state kinetics was assumed in the theory which resulted in a prediction of an increased probability density of events in a transition, when the events are binned according to the angular velocity and angular position. This density is the evidence for the hidden state not detectable in “standard” methods using angular histograms. When plotting the average velocity versus rotation angle, a slow-down in the transition is also due to this short-lived state, which occurs about 40° into the transition with a lifetime of about 20 μs for the PDF1 species All evidence suggest that we discovered an intermediate state very similar to that of the ThF1 species, likely showing a universal mechanism for accelerating ADP release in the ring-shaped F-ATPases. We published the results on one of the ATPases in [Volkán-Kacsó, et al., Proc. Natl. Acad. Sci., USA, 116, 25456 (2019)] and are preparing a publication of the results for the other F1 ATPase in Nature Communications.

3. Electrical Conductivity of Molecular Junctions.
An active field is the electrical conductivity of molecular junctions, both for single molecule and for multilayer systems The theories commonly employed to treat the experimental data are the Landauer theory for coherent electron transfer and the conventional Marcus electron transfer theory. These theories have different domains of validity. Recently a paper by Sowa and coworkers provided a bridge between the two theories using a quantum mechanical treatment that encompassed both coherent and incoherent electron transfer (the incoherence occurs when Marcus theory is applied separately to the electron going from one lead into the molecular junction and then going separately from the junction into the lead at the other end of the molecular Junction, In contrast, in Landauer theory the in and out occurs via a single electronic wave function. It was shown that the two theories are valid at different limits of the current versus voltage curve. We extended the theory of single molecule conductance of Sowa et al. so that it can now also be applied to polar systems. The theory was also made more user-friendly: bye derived it in a simpler way, intended to be more transparent to experimentalists. In the earlier work, the problem was treated quantum mechanically literature using a “spin-boson Hamiltonian” that neglects, as usual, changes in vibration frequency of the environment and hindered rotations of any solvent dipoles.

4. Drude-Smith Electrical Conductivity Equation.
Insight into the Drude-Smith frequency-dependent conductivity equation, which incorporates the effect of back scattering on the electrical conductivity in materials, was obtained by showing how it can be derived using a more general formalism in nonequilibrium statistical mechanics, a “memory function” formalism. The latter has been extensively applied to interpret molecular dynamics results on an analogous process, diffusion in liquids. The present results permitted an extension of the D-S equation to treat a broader array of experimental conditions.

5. Electron-Phonon Interactions in Lead Halide Perovskites.
Lead halide perovskite semiconductors have low-frequency phonon modes within the lead halide sublattice and considered to be important in defining their optoelectronic properties. Electron−phonon coupling governs hot-carrier relaxation, among other important electronic characteristics. Directly observing the interplay between free charge carriers and phonons can provide details on how phonons impact these properties (e.g., exciton populations and other collective modes). We observed the interplay among carriers, phonons, and excitons in mixed-cation and mixed-halide perovskite films by simultaneously resolving the contribution of charge carriers and phonons in these time-resolved terahertz photoconductivity spectra. We also observed the increase in phonon population during carrier cooling and discussed how thermal equilibrium populations of carriers and phonons modulated the carrier transport properties.

6. This history paper was published.

**Training Opportunities:** Dr. Sandor Volkan-Kacso has developed his physical insight and his computer skills during his research here and with his skills has become a faculty member in physics at the nearby Azusa Pacific University. He continues his research on this project with a part-time appointment at Caltech. In this work he has co-written about a half a dozen articles, so improving his skills in statistical data analysis, in developing a theory of these motors and in making original scientific contributions.

Dr. Ricardo Matute, a volunteer on this project with extensive computer skills, has extended the present research further doing molecular dynamics studies of the F-ATPase. He has an academic faculty position at Bernardo O' Higgins University in Santiago Chile.

Dr. Kai Niu, who has an academic faculty position in Tianjin China, has been doing the SFG studies, so extending his skills in computer computations and in analytic methods.

Li Quang Luan was a doctoral candidate at Nanyang Technological University, Singapore, and received from them a fellowship to further his skills in theoretical chemistry and biological motors in our group. He collaborated on writing a paper particularly on the detection of the intermediate state in the ATP hydrolysis

Mr. Oganes Khatchikian, an undergraduate student at Azusa Pacific University during these studies, was a part-time participant in the current project, learning the many-sided aspects of doing research on chemical reaction rate theory and its application to biological motors. He received undergraduate research training at Caltech in this project and was also part of Caltech's SURF (undergraduate) summer program, providing interactions with other SURF students from very different backgrounds.

**Results Dissemination:** The research was described in thirteen talks at symposia and other meetings. Nine papers were published in scientific journals. Two of the articles were published related to electron transfer theory in The Journal of Chemical Physics 2020-2021 celebrating the 65th anniversary of the PI's 1956 electron transfer theory in that journal, the key article in the PI's being awarded the Nobel prize in chemistry. One article was on the early history of the electron transfer theory. A second article was on the single molecule and ensemble electrical conductance of molecular junctions. An article was published on the frequency-dependent terahertz electrical conductivity spectrum of semiconductors and other materials in the journal ChemPhysChem, honoring the late Jean-Michel Savéant. The article was selected for the front cover of the journal issue. The present results were also described at various scientific meetings of American Chemical Society and the Biophysical Society.

**Honors and Awards:** Victor Babes Honorary Scientist Award, Bucharest, Romania, 2018

Medal, Ecole Supérieur du Professorat et de l'Éducation (ESPE); Cergy, France, 2019

Establishment of the Marcus International Managing Award, FLOGEN Organization, Paphos, Cyprus, 2019

Fray International Sustainability Award, FLOGEN Organization, Paphos, Cyprus, 2019

**Protocol Activity Status:**

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**PARTICIPANTS:**

**Participant Type:** PD/PI
**Participant:** Rudolph A Marcus
**Person Months Worked:** 13.00 **Funding Support:**
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**Participant Type:** Staff Scientist (doctoral level)
**Participant:** Sandor Volkan-Kacso
**Person Months Worked:** 10.00 **Funding Support:**

Project Contribution:
National Academy Member: N

**Participant Type:** Staff Scientist (doctoral level)
**Participant:** Kai Niu
**Person Months Worked:** 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Staff Scientist (doctoral level)
**Participant:** Dmitry Shorokov
**Person Months Worked:** 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Undergraduate Student
**Participant:** Oganes Khatchikian
**Person Months Worked:** 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**International Travel:**

| | |
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| ROU | 5 days |
| DEU | 9 days |
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**International Collaboration:**

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**Article Title:** Monitoring Electron-Phonon Interactions in Lead Halide Perovskites Using Time-Resolved THz Spectroscopy
**Authors:** Daming Zhao, Hongwei Hu, Reinhard Haselsberger, Rudolph A. Marcus, Maria-Elisabeth Michel-Beyerl
**Keywords:** perovskite, time-resolved terahertz spectroscopy, phonon, free carrier, exciton
**Abstract:** Lead halide perovskite semiconductors have low-frequency phonon modes within the lead halide sublattice and thus are considered to be soft. The soft lattice is considered to be important in defining their interesting optoelectronic properties. Electron?phonon coupling governs hot-carrier relaxation, carrier mobilities, carrier lifetimes, among other important electronic characteristics. We observe an interplay among carriers, phonons, and excitons in mixed-cation and mixed-halide perovskite films by simultaneously resolving the contribution of charge carriers and phonons in time-resolved terahertz photoconductivity spectra. We observe directly the increase in phonon population during carrier cooling and discuss how thermal equilibrium populations of carriers and phonons modulate the carrier transport properties and reduce the carrier population within band tails. We observe directly the formation of free charge carriers when excitons interact with phonons and dissociate.
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Publication Location:
**Article Title:** Method to extract multiple states in F1-ATPase rotation experiments from jump distributions
**Authors:** Sándor Volkán-Kacsó, Luan Q. Le, Kaicheng Zhu, Haibin Su, Rudolph A. Marcus
**Keywords:** F-ATPase, single-molecule imaging, concerted dynamics, 4-state model, ADP release
**Abstract:** A method is proposed for analyzing fast single-molecule rotation trajectories in F1-ATPase. It uses the distribution of jumps in the rotation angle, and is complementary to the “stalling” technique devised by Noji (2017). It involves multiple states not directly detectable as steps. A bimodal distribution of jumps is observed at certain angles, due to the system being in either of 2 states at the same rotation angle. Using the fluctuations of an imaging probe and 3 states, a theoretical profile of angular jumps is predicted without adjustable parameters. It agrees with experiment for most of the angular range, and agrees at all angles by assuming a fourth state with a 10 micro sec lifetime and a dwell angle about 40° after the ATP binding dwell. The results suggest that ATP binding in one subunit and ADP release from another subunit occur via a transient whose lifetime is 6 orders of magnitude smaller than the lifetime for ADP release from singly occupied F1-ATPase.
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**Article Title:** Sum frequency generation, calculation of absolute intensities, comparison with experiments, and two-field relaxation-based derivation
**Authors:** Kai Niu, Rudolph A. Marcus
**Keywords:** sum frequency generation, integrated spectrum, SFG, motional narrowing, absolute intensities
**Abstract:** The experimental sum frequency generation (SFG) spectrum is the response to an infrared pulse and a visible pulse and is a highly surface-sensitive technique. We treat the surface dangling OH bonds at the air/water interface and focus on the absolute SFG intensities for the resonant terms, a focus that permits insight into the consequences of some approximations. For the polarization combinations, the calculated linewidths for the water interface dangling OH SFG band at 3,700 cm-1 are, as usual, too large, because of the customary neglect of motional narrowing. The integrated spectrum is used to circumvent this problem and justified here using a Kubo-like formalism and theoretical integrated band intensities rather than peak intensities. Only relative SFG intensities are usually reported. The absolute integrated SFG intensities for three polarization combinations for sum frequency, visible, and infrared beams are computed. We use molecular dynamics and the dipole and the polarizability
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Volume: 153 Issue: 21 First Page #: 210401
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Publication Location:
**Article Title:** Reflections on electron transfer theory
**Authors:** Rudolph A. Marcus
**Keywords:** electron transfer, Marcus theory, nonequilibrium dielectric polarization, Franck-Condon principle, isotopic exchange reactions
**Abstract:** Some of the early history leading to the 1956 The Journal of Chemical Physics article on a theory of electron transfer reactions is described. In the development of electron transfer theory in 1956, the simplicity of the final equation for the free energy barrier, after a lengthy and complex derivation, came to me as a surprise. It was indeed a “Eureka” moment, and I give some of its history here.
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Volume: 154 Issue: 3 First Page #: 034110
Date Submitted: 1/25/21 12:00AM Date Published: 1/1/21 8:00AM
Publication Location:
**Article Title:** On the theory of charge transport and entropic effects in solvated molecular junctions
**Authors:** Jakub K. Sowa, Rudolph A. Marcus
**Keywords:** single molecule, molecular conductance, Landauer theory, Marcus theory, entropy of activation, lifetime broadening
**Abstract:** Experimental studies on single-molecule junctions are typically in need of a simple theoretical approach that can reproduce or be fitted to experimentally measured transport data. In this context, the single-level variant of the Landauer approach is most commonly used, but methods based on Marcus theory are also gaining popularity. Recently, a generalized theory unifying these two approaches has also been developed. In this work, we extend this theory so that it includes entropic effects, which can be important when polar solvents are involved. We investigate the temperature-dependence of the electric current and compare it to the behavior predicted by the Landauer and the conventional Marcus theory. The generalized theory provides a simple framework for understanding charge transport through molecular junctions. We explore the role of the entropic effects in different transport regimes and suggest experimental criteria for detecting them in molecular junctions.
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**Article Title:** The Drude-Smith Equation and Related Equations for the Frequency-Dependent Electrical Conductivity of Materials: Insight from a Memory Function Formalism
**Authors:** Rudolph Arthur Marcus, Wei-Chen Chen
**Keywords:** Drude-Smith equation, electrical conductivity, frequency dependence, disordered materials, semiconductors, back scattering, memory function
**Abstract:** The Drude-Smith equation is widely used for treating the frequency-dependent electrical conductivity of materials in the terahertz region. An attractive feature is its sparsity of adjustable parameters. A significant improvement over Drude theory for these materials, the theory includes backscattering of the charge carriers. It has nevertheless been criticized, including by Smith himself, because of the arbitrariness of a step in the derivation. We recall a somewhat similar behavior of back scattering in fluids observed in molecular dynamics computations and discussed in terms of memory functions. We show how theories such as Drude-Smith and Cocker et?al. are examples of a broader class of theories by showing how they also arise as particular cases of a memory function formalism that divides the interactions into short and long range.
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## RPPR Final Report
as of 26-Oct-2022

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Publication Location:

**Article Title:** Biographical Background and Front Cover Description for The Drude-Smith Equation and Related Equations for the Frequency-Dependent Electrical Conductivity of Materials: Insight from a Memory Function Formalism

**Authors:** Wei-Chen Chen, Rudolph A. Marcus

**Keywords:** Drude-Smith equation, electrical conductivity, frequency dependence, disordered materials, back scattering, memory function, history

**Abstract:** This report describes the background of the authors and of this research on the Drude-Smith equation that is widely used for treating the frequency-dependent electrical conductivity of materials in the terahertz region. The article was selected for the front cover for the journal ChemPhysChem for the issue honoring the late electrochemist Jean-Michel Saveant.

**Distribution Statement:** 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info

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**Partners**

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I certify that the information in the report is complete and accurate:

Signature: Rudolph A. Marcus

Signature Date: 8/5/22 7:11PM

W911NF1810070: Novel Surface Phenomena
Reporting Period: January 15, 2018 – January 14, 2022
Rudolph A. Marcus

## Summary of Accomplishments

1. Successfully showed agreement between computed and experimentally observed integrated intensity for sum frequency generation spectrum of dangling OH bonds at a water surface.
2. Computed with no adjustable parameters ATP binding/ATP exiting angle dependent rate constants for controlled rotation experiments using data from independent stalling, free rotation and ensemble biochemical experiments with no adjustable parameters.
3. Developed a method for determining previously unobserved short-lived hidden states in the ATP hydrolysis cycle in the enzyme F1 ATPase.
4. Successfully extended single molecule conductivity theory that treats experimentally observed single molecule conductance so as to include entropic effects.
5. Placed the most commonly used theory, the Drude-Smith theory, to treat terahertz conductivity of somewhat disordered materials in a broader context so as to better understand its relation to other theories.