Final Progress Report
Sustainability Science Program, Harvard University
Term: September 1, 2010 – August 31, 2011
Submitted: July 2011

Name: Roberto Olivares-Amaya

Your field(s):
chemistry, physics

Your degree program, institution and (expected) graduation date:
PhD, Chemical Physics, Harvard University, expected May 2012

Faculty host(s) at Harvard name and department:
Alán Aspuru-Guzik, Dept. of Chemistry and Chemical Biology;
Venkatesh Narayanamurti, School of Engineering and Applied Sciences

Description of SSP-related research activity:

Title: Mixed-Metal Surface Enhanced Raman Scattering: Towards a New Approach for Monitoring Water Pollution

Abstract: Global food demand continues to grow to keep up-to-speed with population increase and dietary shifts related with a higher standard of living. Relatedly, the use of pesticides is also increasing in rapidly developing countries. This presents itself as a prevalent health threat that affects farmers directly, but also impacts the rest of the population as externalities. Current options for identifying noxious substances rely on laboratory use or portable sensors that can find only one component at a time. We propose a mixed-metal method to surface enhanced Raman scattering (SERS), which will be applicable to the design of sensors for trace analysis of pollutants. These sensors will be able to identify simultaneously multiple trace compounds of both inorganic and organic compounds, as is the case of arsenic and pesticides, respectively. SERS reveals the vibrations of molecules, which makes it possible to identify these substances in a complex mixture. Although SERS is a very powerful technique, it lacks specificity. In this study, we explore the interaction of transition metal monolayers over the typical SERS substrate and prove it leads to larger signals and improved specificity. The latter property is relevant to measure different substances at a time. We use theoretical and computational methods to understand the interactions between molecules and mixed-metal. At first generic substances are used to reduce the complexity of the problem, but we later aim to study pesticides and some noxious byproducts. The theoretical approach is linked to an experimental collaboration with the Eric Mazur Group at Harvard where they manufacture and prove that the mixed metal approach is feasible. Looking ahead, we aim for the rational design of a portable device which can intrinsically separate and measure trace concentrations of molecules. This tool would be a fundamental step towards efficiently measuring harmful substances in the field and the laboratory.

Identification of the problem you address:
Current options for identifying noxious substances rely on laboratory use or portable sensors that can find only one component at a time. At the same time, the SERS method, although powerful, lacks the specificity that can make it a general tool in the field.

Key question asked about the problem:
Will the use of different transition metal monolayers aid in the selectivity of SERS? If so, will this 'mixed-metal' technique be able to be a useful tool in the field for identification of pesticides?

The methods by which you answered that question:
We answer the question through theoretical and computational methods showing that these monolayers can provide specificity. We further validate this claim by collaborating with experimentalists, who built a device that reasonably matched the theoretical predictions.

Principle literature upon which the research drew:

SERS Literature
- M. Fleischmann, *et al.*, *Chem. Phys. Lett.*, 1974, **26**, 163.
- L. Jensen, *et al.*, *Chem. Soc. Rev.*, 2008, **37**, 1061.
- M. Mulvihill, *et al.*, *Angew. Chem. Int. Ed. Engl.*, 2008, **47**, 6456

Environmental SERS Literature
- T. Pradeep, *Thin Solid Films*, 2009, **517**, 6441
- Álvarez-Puebla, et al., *Energy Environ. Sci.*, 2010, **3**, 1011
- P. Aldeanueva-Potel, et al., *Anal. Chem.*, 2009, **81**, 9233

Water, Sanitation and Monitoring
- WHO and UNICEF Joint Monitoring Programme for Water Supply and Sanitation, Progress on Drinking Water and Sanitation:
- Special Focus on Sanitation, *World Health Organization*, 2008.
- World Health Organization, Guidelines for Drinking-Water Quality, **Vol. 1**, 2008.
- S. D. Richardson, *Anal. Chem.*, 2009, **81**, 4645

Empirical data acquisition description:
N/A

Geographical region studied:
N/A

Recommendations that might be relevant for your problem:
The work was very academic in nature, since the research still is at an early stage. It would be very beneficial to start collaborating/speaking with people at several NGOs (*e.g.*, Gates Foundation, WHO) for feedback.

A description of the final product(s) you have/are aiming to produce:
We are currently writing a joint theory and experiment article which will be aimed to appear in Nano Letters

Description of major other intellectual or professional advancement activity(ies) over the past academic year:
This research will become a chapter in my PhD dissertation.

Please list citations for reports, papers, publications and presentations that built on your fellowship research:

Published
R. Olivares-Amaya, M. Stopa, X. Andrade, M.A. Watson, A. Aspuru-Guzik, Anion Stabilization in Electrostatic Environments, *Journal of Physical Chemistry Letters*, 2, 682-688 **(2011)**
Excess charge stabilization of molecules in metallic environments is of particular importance for fields such as molecular electronics and surface chemistry. We study the energetics of benzene and its anion between two metallic plates. We observe that orientational effects are important at small interplate separation. This leads to benzene oriented perpendicular to the gates being more stable than the parallel case due to induced dipole effects. We find that the benzene anion, known for being unstable in the gas phase, is stabilized by the plates at

zero bias and an interplate distance of 21 Å. We also observe the effect of benzene under a voltage bias generated by the plates; under a negative bias, the anion becomes destabilized. We use the electron localization function to analyze the changes in electron density due to the bias. These findings suggest that image effects such as those present in nanoscale devices are able to stabilize excess charge and should be important to consider when modeling molecular transport junctions and charge-transfer effects.

D.G. Tempel, M.A. Watson, R. Olivares-Amaya, A. Aspuru-Guzik, Time-dependent density functional theory of open quantum systems in the linear-response regime, *Journal of Chemical Physics*, 134, 074116 **(2011)**
Time-dependent density functional theory (TDDFT) has recently been extended to describe many-body open quantum systems evolving under nonunitary dynamics according to a quantum master equation. In the master equation approach, electronic excitation spectra are broadened and shifted due to relaxation and dephasing of the electronic degrees of freedom by the surrounding environment. In this paper, we develop a formulation of TDDFT linear-response theory (LR-TDDFT) for many-body electronic systems evolving under a master equation, yielding broadened excitation spectra. This is done by mapping an interacting open quantum system onto a noninteracting open Kohn–Sham system yielding the correct nonequilibrium density evolution. A pseudoeigenvalue equation analogous to the Casida equations of the usual LR-TDDFT is derived for the Redfield master equation, yielding complex energies and Lamb shifts. As a simple demonstration, we calculate the spectrum of a C2 + atom including natural linewidths, by treating the electromagnetic field vacuum as a photon bath. The performance of an adiabatic exchange-correlation kernel is analyzed and a first-order frequency-dependent correction to the bare Kohn–Sham linewidth based on the Görling–Levy perturbation theory is calculated.

Submitted

R. Olivares-Amaya, C. Amador-Bedolla, J. Hachmann, S. Atahan-Evrenk, R.S. S\'anchez-Carrera, L. Vogt, A. Aspuru-Guzik, Accelerated computational discovery of high-performance materials for organic photovoltaics by means of cheminformatics, **Submitted (2011)**
In this perspective we explore the use of strategies from drug discovery, pattern recognition, and machine learning in the context of computational materials science. We focus our discussion on the development of donor materials for organic photovoltaics by means of a cheminformatics approach. These methods enable the development of models based on molecular descriptors that can be correlated to the important characteristics of the materials. Particularly, we formulate empirical models, parametrized using a training set of donor polymers with available experimental data, for the important current-voltage and efficiency characteristics of candidate molecules. The descriptors are readily computed which allows us to rapidly assess key quantities related to the performance of organic photovoltaics for many candidate molecules. As part of the Harvard Clean Energy Project, we use this approach to quickly obtain an initial ranking of its molecular library with 2.6 million candidate compounds. Our method reveals molecular motifs of particular interest, such as the benzothiadiazole and thienopyrrole moieties, which are present in the most promising set of molecules.

J. Hachmann, R. Olivares-Amaya, S. Atahan-Evrenk, C. Amador-Bedolla, R.S. S\'anchez-Carrera, A. Gold-Parker, L. Vogt, A.M. Brockway, A. Aspuru-Guzik, The Harvard Clean Energy Project: Large-scale computational screening and design of organic photovoltaics on the World Community Grid, **Submitted (2011)**
This perspective article introduces the Harvard Clean Energy Project (CEP), a theory driven search for the next generation of organic solar cell materials. We give an overview of its setup and infrastructure, present first results, and outline upcoming developments.
CEP has established an automated, high-throughput, in silico framework to study potential candidate structures for organic photovoltaics. The current project phase is concerned with thecharacterization of millions of molecular motifs using first-principles quantum chemistry. The unprecedented scale of this study requires a correspondingly large computational resource which is provided by distributed volunteer computing on IBM's World Community Grid. The results are compiled and analyzed in an extensive reference database and will be made available for public use. In addition to finding specific candidates with certain properties, it is the goal of CEP to illuminate and understand the structure-property relations in the domain of organic electronics. Such insights can open the door to a rational and systematic design of future high-performance materials. The

computational work in CEP is tightly embedded in a collaboration with experimentalists which provide valuable input and feedback to the project.

In Preparation

R. Olivares-Amaya, D. Rappoport, P. Muñoz, P. Peng, E. Mazur, A. Aspuru-Guzik, On Mixed-Metal Surface-Enhanced Raman Scattering, **In preparation (2011)**

We present a mixed-metal surface-enhanced Raman scattering (MM-SERS) approach. This involves a typical SERS gold or silver substrate and a transition metal overlayer which is known to interact with the analyte more strongly than the coinage metal. This SERS scheme goes beyond the borrowing SERS approach developed in the past to one where the transition metal monolayer lends Raman enhancement via the chemical effect. The development of this technique will aid a wide array of molecules have a homogeneously large Raman enhancement and be a useful tool towards SERS instrumentation.

Principal collaborators outside Harvard:

Prof. Carlos Amador-Bedolla, Facultad de Química, Universidad Nacional Autónoma de México

List any awards or grants that you have received this year for the current or coming year:

American Conference on Theoretical Chemistry Travel Fellowship, *Chemical Effects in Surface-Enhanced Raman Scattering.* Contributed Poster at American Conference on Theoretical Chemistry. Telluride, CO (July, 2011)

Materials for Energy Applications Travel Fellowship, *Finding Organic Photovoltaic Materials One Screensaver at a Time.* Contributed Poster at USC-DOE Conference on Materials for Energy Applications: Experiment, Modeling and Simulations. Rancho Palos Verdes, CA (March, 2011)