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Project Title: The Role of Electronic Excitations on Chemical Reaction Dynamics at Metal, Semiconductor and Nanoparticle Surfaces
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Summary of Accomplishments:

Electronic Friction Theory for Molecules at Metal Surfaces

Molecular adsorbates on metal surfaces exchange energy with substrate vibrational modes (phonons) and low-lying electron-hole pair (EHP) excitations. EHP excitations can dissipate energy such that in the limit of weak coupling, EHPs can be seen as exerting frictional forces on adsorbates that enhance energy transfer and facilitate vibrational relaxation or hot-electron mediated chemistry. The underlying framework for this theory, "Molecular Dynamics with Electronic Friction", was developed previously by the PI, in collaboration with Martin Head-Gordon [M. Head-Gordon and J. C. Tully, *J. Chem. Phys*. **103**, 10137, (1995)]. Expressions were derived for computing the frictional forces by ab initio electronic structure or density functional theory (DFT) methods. However, this formulation requires extrapolating nonadiabatic couplings computed from a finite number of discrete electronic levels to the true continuum of states representative of a metal. Several methods for doing this have been proposed by different research groups, but all have suffered from spurious dependences on basis sets, incomplete convergence, and empirical smoothing. As an example, calculations of the vibrational lifetime of the CO molecule on a copper surface by different methods differ by a factor of 5.

Our work over the last three years has largely eliminated these problems. We now have a robust method that we are implementing in a number of DFT codes, making ab initio Molecular Dynamics with Electronic Friction a practical and accurate tool for simulating chemical dynamics at metal surfaces. The method is based on Kohn-Sham density functional theory for condensed phase and cluster systems [Publication 7]. Using local atomic-orbital basis sets, we calculate nonadiabatic coupling matrix elements and evaluate the full electronic friction tensor in the Markov (no memory) limit. Our approach is numerically stable, as shown by a detailed convergence analysis. We furthermore benchmarked the accuracy of our approach by calculation of vibrational relaxation rates and lifetimes for a number of diatomic molecules at metal surfaces, with comparison to experiments.

For the first time, we have computed the full electronic friction tensor [Publication 6]. The friction tensor (6x6 matrix for a diatomic molecule with 6 degrees of freedom) quantifies the magnitudes of the friction on different types of motion (diagonal elements), as well as the friction-induced coupling between different motions (off-diagonal elements). We show that the friction tensor is generally anisotropic and

nondiagonal, as found for the hydrogen atom on the Pd(100) surface and the CO molecule on the Cu(100) surface. Our initial applications to diatomic molecules interacting with metal surfaces demonstrate that, in contrast to prior assumptions, the 6x6 friction tensor is not diagonal in normal mode coordinates; i.e., the electronic friction introduces relatively strong coupling between different normal modes of vibration. This implies that electron-hole pair induced nonadiabatic coupling at metal surfaces leads to friction-induced mode coupling, therefore, opening an additional channel for energy redistribution. Note that the most widely used method for computing electronic friction, based on a free electron gas local density approximation, completely neglects the tensorial property of the friction and therefore the resulting mode dependence and coupling.

Most recently, we have applied our methodology to the scattering and dissociative chemisorption of H_2 on the Ag(111) surface [Publication 9]. We find strong mode dependence and a dominance of nonadiabatic energy loss along the H—H bond stretch coordinate for both scattering and dissociative chemisorption. Exemplary trajectories with varying initial conditions indicate that this mode-specificity translates into modulated energy loss during a dissociative chemisorption event. The directionality of frictional forces induces dynamical steering that affects individual reaction outcomes, specifically for low-incidence energies and vibrationally excited molecules. Mode-specific friction induces enhanced loss of rovibrational rather than translational energy and should be most visible in its effect on final energy distributions in molecular scattering experiments.

The Influence of Phase Transitions on Chemical Reaction Rates

In collaboration with Prof. Elsa Yan (Yale University) and Prof. Victor Batista (Yale University), we studied the thermal rate of isomerization of the 11-cis retinyl chromophore in the visual pigment rhodopsin, *in the absence of light*. The motivation for this study was to put limits on the dark noise, i.e., the background signal that limits vision in dim light. In the course of this study the Yan group made a remarkable discovery: at temperatures between 52.0 and 64.6°C, the measured rate constants fit well to an Arrhenius straight line with, however, an unexpectedly large activation energy of 114 ± 8 kcal/mol, much larger than the 60 kcal/mol photoactivation energy at 500 nm. Moreover, they obtained an unprecedentedly large prefactor of $10^{72 \pm 5}$ s^{-1}, about 45 orders of magnitude larger than any previously reported prefactor for a localized unimolecular reaction and 60 orders of magnitude larger than typical frequencies of molecular motions! At lower temperatures the measured Arrhenius parameters were found to be more normal: E_a = 22 ± 2 kcal/mol and $A_{pref} = 10^{9\pm 1}$ s^{-1} in the range 37.0 – 44.5°C. These results were published in 2014 [Publication 1], along with the working hypothesis that the reaction barrier is somewhat lower when the protein is disordered or melted than when the chromophore is more constrained in the folded state of the protein. This barrier lowering produces a driving force to lower the melting temperature when the system is constrained at the transition state. If the initial state is ordered and the transition state is partially or completely melted, according to transition state theory, there will be huge increases in both the enthalpy and entropy of activation. At lower temperatures where both the initial and transition states are ordered, the activation energy and entropy will be more normal, producing a distinct “elbow” in the Arrhenius plot, as observed.

We have since made advances both in experiment (Yan group) and theory (Tully, supported by this DOE-BES grant) [Publication 8]. In order to confirm the hypothesis that the high activation energy and prefactor arise from a partial or complete melting transition, rate measurements were carried out on two rhodopsin mutants that were selected because they exhibit some disruption of the hydrogen bonding network, resulting in a lowering of the melting temperature. Our main theoretical contribution was to develop a two-state (ordered and disordered) model to predict the striking non-Arrhenius behavior, including the dramatic elbow and unprecedented prefactor observed at higher temperatures. In its simplest form, the model requires only 4 parameters, the enthalpy and entropy of disordering the protein (correlated with its enthalpy and entropy of melting), the barrier to reaction when ordered, and the barrier to reaction when disordered. Optimizing these parameters provides an excellent, quantitative fit to the experimental results, including the observed differences between WT rhodopsin and the mutants. The model is certainly too simplified to expect quantitatively accurate predictions without adjustment of parameters. A number of possible factors are missing from the model, including partial disorder rather than complete melting, recrossing corrections and/or Kramer's friction at the transition state, the existence of special hydrogen bonds that couple more strongly to the chromophore, etc. Nevertheless, this represents a conclusive demonstration of the phase transition origin of these remarkable results. This behavior may well prove to be quite general, not only in biological reactions, but also in condensed phase and surface reactions carried out at temperatures and pressures close to 2 or 3 dimensional phase transitions.

Scattering of Nitric Oxide from the Au(111) Surface.

Previously under support from this DOE-BES grant we developed a computational method called "Independent Electron Surface Hopping" (IESH) to simulate the interactions of molecules with metal surfaces in cases in which electron transfer events occur [N. Shenvi, S. Roy, and J. C. Tully, *J. Chem. Phys*. **130**, 174107 (2009)]. In such cases the electronic friction method described above is not applicable – the weak coupling approximation that underlies the electronic friction theory becomes invalid. We successfully tested the IESH method by comparison with experiments carried out by the group of Alec Wodtke (Göttingen, Germany) on the scattering of vibrationally excited NO molecules from the (111) surface of a gold crystal. The IESH theory provided a very good description of the experimental results, from which valuable insights were extracted. However, the experiments were carried out at low incident translational energy (0.05 eV) and the NO molecules were excited only to a single vibrational level, $v = 15$. More recently, the Wodtke group has carried out a more complete set of experimental studies of NO scattered from Au(111) for a wider range of incidence translational and initial vibrational quantum numbers. We have carried out extensive IESH simulations for the new experimental conditions [Publication 2]. We find that the IESH calculations are no longer in good agreement with the experimental results. Through an exhaustive exploration of the sensitivity of results to various components of the theory, we have found that the problem is not with the IESH theory itself. Rather, the main source of discrepancy is inaccuracy of the underlying NO-Au(111) potential energy surface that was employed in the simulations. This is an important finding for future applications of IESH.

Intermolecular Interactions from Charge Populations

We introduced a system-independent method to derive effective atomic C-6 coefficients and polarizabilities in molecules and materials purely from charge population analysis [Publication 5]. This enables the use of dispersion-correction schemes in electronic structure calculations without recourse to electron-density partitioning schemes and expands their applicability to semi-empirical methods and tight-binding Hamiltonians. We show that the accuracy of our method is on a par with established electron-density partitioning based approaches in describing intermolecular C-6 coefficients as well as dispersion energies of weakly bound molecular dimers, organic crystals, and supramolecular complexes. We showcase the utility of our approach by incorporation of the recently developed many-body dispersion method [Publication 3] into the semi-empirical density functional tight-binding method and propose the latter as a viable technique to study hybrid organic-inorganic interfaces

References to Publications of DOE-Sponsored Research: 2014-2017

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