

O 27: Surface Dynamics: Theory

Time: Tuesday 10:30–12:30

Location: TRE Phy

Invited Talk

O 27.1 Tue 10:30 TRE Phy
The role of nonadiabatic friction in chemical dynamics at metal surfaces — ●REINHARD MAURER — Department of Chemistry, Yale University, New Haven CT 06520, USA

Despite a large mass discrepancy, hydrogen atoms show inelastic scattering from metal surfaces and, despite vibrational decoupling of intramolecular stretch motion from substrate phonons, adsorbate vibrations are damped efficiently on metals. Both of these effects can be attributed to low-lying electronic excitations or "hot electrons" in the metal substrate that interact with the adsorbate via nonadiabatic coupling. The importance of such effects in elementary processes in surface photophysics, molecular device physics, heterogeneous photocatalysis and ultrafast reaction dynamics motivates the development of efficient first-principles electronic structure methods that account for coupled electron-nuclear dynamics in materials. On examples ranging from hydrogen scattering to vibrational energy dissipation and molecular switching at metal surfaces, I will present our Density-Functional Theory-based approach to describe nonadiabatic effects in two limiting regimes, the surface hopping and the electronic friction regime. In comparison with experiment and current state-of-the-art simulation methods, we find a qualitatively correct description of nonadiabatic effects for a variety of systems. In combining our method with mixed quantum-classical molecular dynamics, I will show how nonadiabatic friction affects the reaction dynamics and contributes to adsorbate-substrate energy transfer.

O 27.2 Tue 11:00 TRE Phy
Non-adiabatic vibrational damping of molecular adsorbates: Beyond electronic friction — ●SIMON P. RITTMAYER¹, JÖRG MEYER², and KARSTEN REUTER¹ — ¹Technische Universität München — ²Universiteit Leiden

The availability of low-energy electron-hole (*eh*) pair excitations generally questions the validity of the ubiquitous Born-Oppenheimer approximation for adsorbate dynamics on metal surfaces. An in-depth scrutiny thus requires to consider the non-adiabatic coupling of nuclear motion to these *eh*-pair excitations. Unfortunately, an explicit calculation from first principles remains a formidable challenge. Electronic friction theory is very popular to capture the effects of the non-adiabatic energy loss on the nuclear dynamics in a computationally convenient way. This avoids explicit electron dynamics and concomitant ultrafast time scales, but for these reasons also precludes a more fundamental understanding of the underlying *eh*-pair excitations.

In this situation, we advance a perturbative approach rooted in time-dependent density-functional theory which allows to actually evaluate *eh*-pair excitation spectra [1]. Applying this to non-adiabatic vibrational damping of CO on Cu(100) and Pt(111), we find that the non-adiabatic energy loss obtained from our spectra is consistent with experimentally measured lifetimes. Moreover, we discuss intriguing deviations from the linear relationship between non-adiabatic energy loss and kinetic energy predicted by electronic friction theory that might be measurable in new experiments.

[1] J. Meyer and K. Reuter, New. J. Phys. **13**, 085010 (2011).

O 27.3 Tue 11:15 TRE Phy
Quantization of collective excitations in finite systems: An ab initio quasiparticle picture for hot carrier generation in noble metal nano clusters — ●MIKAEL KUISMA^{1,2}, TUOMAS ROSSI³, and PAUL ERHART² — ¹University of Jyväskylä, Jyväskylä, Finland — ²Chalmers University of Technology, Gothenburg, Sweden — ³Aalto University, Helsinki, Finland

Resolving hot electron generation from coherent collective plasmon excitations in nanoparticles is a vital step in understanding a wide variety of physical processes. However, in order to facilitate a quantitative understanding of hot electron generation, a physically sound picture of collective excitations in nanoparticles must be established.

In our time-dependent density functional theory and many body perturbation theory based framework we extract the collective coordinates of plasmons in the electron-hole space. We find that a discrete, topology dependent number of electron-hole pairs is collectively involved in formation of a plasmon. The collective coordinates define the bare plasmons, which are further renormalized due to other electron-hole excitations via the plasmon self energy. The emerging quasiparticle

picture is able to explain the plasmon renormalization due to Landau scattering and d-band screening in noble metal nanoparticle with unprecedented simplicity in reasoning and intuition, while maintaining the *ab initio* quantitative nature of the calculation. In order to demonstrate our approach, we analyze hot-electron generation rates in gold clusters.

O 27.4 Tue 11:30 TRE Phy
Insights of the Ultrafast Charge Transfer Process in CdSe Quantum Dot/Organic Molecule System: A Real-Time Time-Dependent Ab Initio Study — ●ZHI WANG¹, JAN-PHILIP MERKL¹, MONA RAFIPOOR¹, HOLGER LANGE¹, LIN-WANG WANG², and GABRIEL BESTER¹ — ¹Institut für Physikalische Chemie, Universität Hamburg — ²Material Science Division, Lawrence Berkeley National Laboratory

We report for the first time a real-time time-dependent density function theory (rt-TDDFT) simulation on experimental size CdSe quantum dot/organic molecule system, to analyze its ultrafast (femtosecond to sub-picosecond) photoexcited charge transfer (CT) dynamics. Non-adiabatic dynamic details, such as the size-dependence of CT process, the carrier separation and cooling, the electron-phonon interaction and Auger-assisted process are presented using our high-efficient rt-TDDFT package. Our results are in excellent agreement with experiment data.

O 27.5 Tue 11:45 TRE Phy
Importance of many-body dispersion and temperature effects on gas-phase gold cluster (meta)stability — ●BRYAN R. GOLDSMITH, PHILIPP GRUENE, JONATHAN T. LYON, DAVID M. RAYNER, ANDRÉ FIELICKE, MATTHIAS SCHEFFLER, and LUCA M. GHIRINGHELLI — Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

Gold clusters in the gas phase exhibit many structural isomers that are shown to interconvert frequently, even at room temperature. We performed ab initio replica-exchange molecular dynamics (REMD) calculations on gold clusters (of sizes 5-14 atoms) to identify metastable states and their relative populations at finite temperature, as well as to examine the importance of temperature and van der Waals (vdW) on their isomer energetic ordering. Free energies of the gold cluster isomers are optimally estimated using the Multistate Bennett Acceptance Ratio. The distribution of bond coordination numbers and radius of gyration are used to address the challenge of discriminating isomers along their dynamical trajectories. Dispersion effects are important for stabilizing three-dimensional structures relative to planar structures and brings isomer energetic predictions to closer quantitative agreement compared with RPA@PBE calculations. We find that higher temperatures typically stabilize metastable three-dimensional structures relative to planar/quasiplanar structures. Computed IR spectra of low free energy Au₉, Au₁₀, and Au₁₂ isomers are in agreement with experimental spectra obtained by far-IR multiple photon dissociation in a molecular beam at 100 K.

O 27.6 Tue 12:00 TRE Phy
Replica-Exchange Grand-Canonical Algorithm for Determining Phase Diagrams of Surfaces in Reactive Atmospheres — ●YUANYUAN ZHOU, LUCA M. GHIRINGHELLI, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

A temperature-pressure phase diagram describes the composition and structure of a system at thermal equilibrium and is an essential tool for understanding material properties. The atomistic thermodynamics (AT) approach has been very successful in predicting phase diagrams for surfaces [K. Reuter, M. Scheffler, PRL **90**, 046103 (2003)] and gas-phase clusters [S. Bhattacharya *et al.*, PRL **111**, 135501 (2013)] at realistic *T, p* conditions. However, its limitation is the lack of an unbiased sampling of the configurational space. Here, we present a novel replica-exchange (RE) grand-canonical (GC) Monte-Carlo (MC) algorithm that allows for the efficient estimate of the partition function of atomistic systems. We specifically target open systems in the GC ensemble, aiming at describing (nano)structured surfaces in a reactive atmosphere (e.g., for heterogeneous catalysis) at realistic *T, p*. RE allows for an efficient sampling by shuttling configurations from regions of low *T* or high chemical potential (μ) to regions of high *T* or low

μ . In order to demonstrate the approach, we apply REGC-MC to a two-component Lennard-Jones system with a surface in contact with a gas-phase. In particular, we discuss REGC-MC's viability by comparing our results with calculated ones using AT and find good agreement at low coverage but quite different at relatively high coverage.

O 27.7 Tue 12:15 TRE Phy

Theoretical description of Ge(001) surface reconstruction

— •KATHARINA NOATSCHK^{1,2}, WOLFGANG KLESSE², THOMAS SCHROEDER^{1,2}, and GÖTZ SEIBOLD¹ — ¹Brandenburg Technical University Cottbus-Senftenberg, 03046 Cottbus, Germany — ²IHP-Innovations for High Performance Microelectronics, 15236 Frankfurt(Oder), Germany

In our work we study the reconstruction of the Ge(001) surface within the Ising model. Due to the reduced bonding of surface atoms ad-

jacent germanium surface atoms tend to form so-called tilted dimers [1]. Experimentally one observes at low temperature the $c(4 \times 2)$ structure which corresponds to an alternating tilt pattern whereas at high temperature the overall tilt vanishes. In addition to the $c(4 \times 2)$ structure experimental and theoretical work also indicates the presence of an intermediate $p(2 \times 2)$ structure with alternating tilts only along one crystallographic axis whereas it is constant along the other. In our investigations we represent the two tilt directions of a dimer by an Ising spin and take the interaction parameters between Ising variables from first principle calculations [2]. We evaluate the phase diagram for the various dimer order parameters within a Metropolis algorithm. Moreover, we obtain from the Monte Carlo simulation domains on the surface which are consistent with the experimental measurements.

[1] D.J. Chadi, Phys. Rev. Lett. 43 (1979) 43

[2] Y. Yoshimoto, et al. Phys. Rev. B 61 (2000) 1965