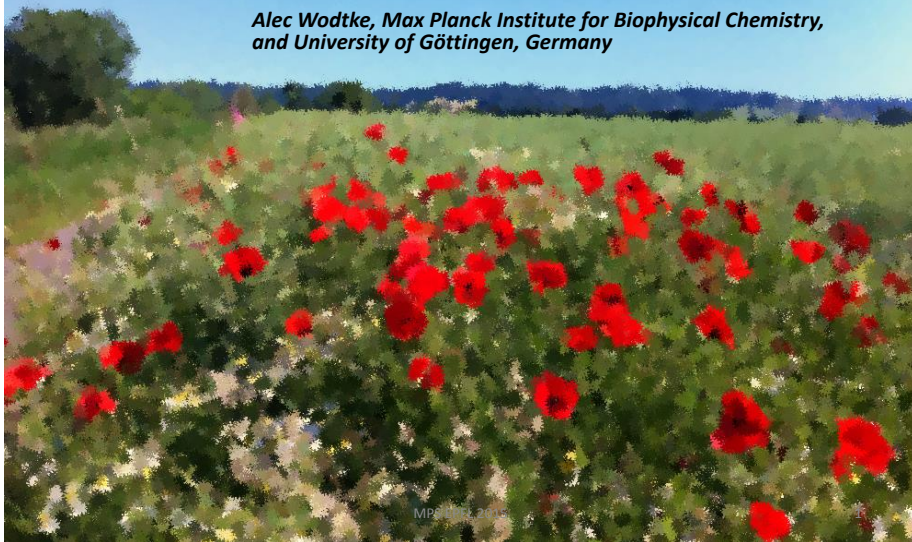


A Dynamical Approach to Surface Chemistry

Summer school of the Max Planck EPFL Center on Molecular Nanoscience and Technology

Alec Wodtke, Max Planck Institute for Biophysical Chemistry, and University of Göttingen, Germany



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“Scientists should always state the **assumptions** upon which their facts are based.”

Author Unknown

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Outline of the talk

- Motivation and Background: The provisional model of surface chemistry
- Mechanism of H-atom sticking at a metal surface: An electronically nonadiabatic reaction occurring in high dimension
- Measuring accurate thermal rates of surface reactions: New experimental approaches to old problems in surface chemistry

Producing ultrashort H atom pulses

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Chemistry is a problem in quantum mechanics

$$\mathcal{H}_{\text{molecular}} = -\sum_{i=1}^N \frac{\hbar^2}{2M_i} \nabla_{R_i}^2 - \sum_{i=1}^n \frac{\hbar^2}{2m_i} \nabla_{r_i}^2 - \sum_{i,j}^{N,n} \frac{Z_i e^2}{|R_i - r_j|} + \sum_{i,j,i < j}^n \frac{e^2}{|r_i - r_j|} + \sum_{i,j,i < j}^N \frac{Z_i Z_j e^2}{|R_i - R_j|}$$



It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed...

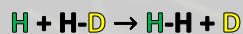
PAM Dirac, Proceedings of the Royal Society of London. Series A Vol. 123, No. 792 (1929), pp. 714-733

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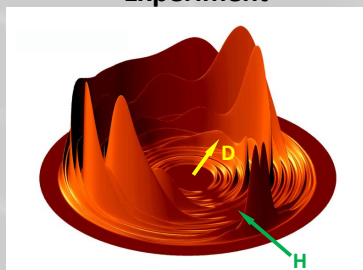
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Standard Model of Chemical Reactivity

Calculate the quantum motion of nuclei using accurate potential energy surface within the Born-Oppenheimer Approximation



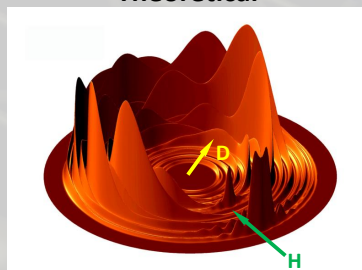
Experiment



Using Rydberg atom tagging

Yang and Skodje, Journal of Chemical Physics, 117 (18) 8341-8361 (2002)

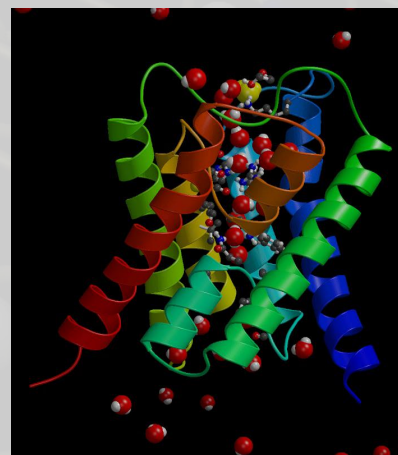
Theoretical



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Another approach to „seeing“ the atomic world: Born-Oppenheimer simulation



- Pathway of a water molecule through AQP1. Ribbon representation of one aquaporin-1 monomer and a selection of water molecules.
- One water molecule, colored yellow, finds its way completely through the pore.
- Those side-chains that are in direct contact with passing water molecules are shown explicitly.

The world's greatest microscope?

B. L. de Groot and H. Grubmüller: Science 294, 2353-2357 (2001)

6

Theoretical challenges for chemistry metal surfaces compared to small molecule reactions

- **Electronic structure problem is more difficult**
 - Density Functional Theory becomes the method of choice
 - Usually at the GGA level
- **Born-Oppenheimer Approximation may fail**
 - Models of electronic nonadiabaticity are needed
- **Many (many) degrees of freedom involved**
 - Constructing potential energy surfaces is challenging
 - Direct Dynamics has become popular
 - Classical mechanics is often assumed

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Provisional Model of Surface Chemistry: Key approximations

Its best to consider an example

1. Born-Oppenheimer Approximation
2. The Density Functional Theory (Generalized gradient approximation)
3. Classical Approximation for Nuclear Motion
4. Reduced dimension approximations are often introduced

See *The dynamics of molecular interactions and chemical reactions at metal surfaces: Testing the foundations of theory*, Nils Bartels, Kai Golibrzuch, Daniel J. Auerbach, Alec M. Wodtke, *Annual Review of Physical Chemistry*, 66, 399-425, (2015),

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The Mechanism of H atom adsorption at a metal surface

The importance of electronic nonadiabaticity

The provisional model applied to H-atom adsorption

Binary collision model

$$m_1 v_1 = -m_1 v_1' + m_2 v_2'$$

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_1 v_1'^2 + \frac{1}{2} m_2 v_2'^2$$

$$E' = \text{trans. energy retained}$$

$$= v_1'^2 / v_1^2$$

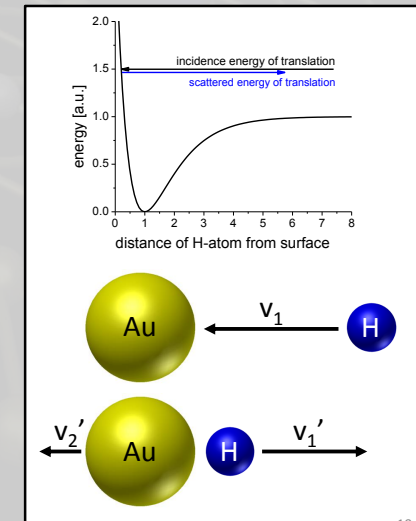
$$= (m_1 - m_2)^2 / (m_1 + m_2)^2$$

$$m_1 = 1 \text{ (H)}$$

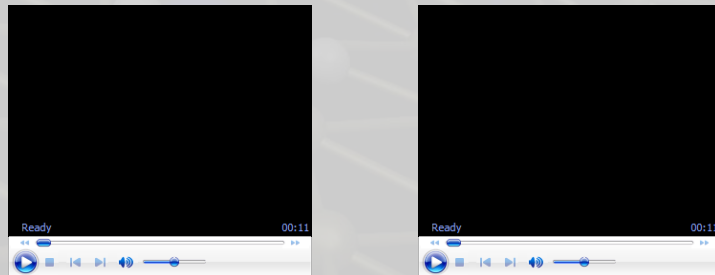
$$m_2 = 197 \text{ (Au)}$$

$$E' = 0.98 \times E$$

$$E' = (m_1 - m_2)^2 / (m_1 + m_2)^2$$



Direct Dynamics applied to H-atom Adsorption on Au(111): „Duck diving“ collisions



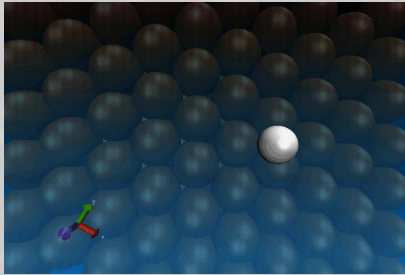
- Ab initio Molecular Dynamics (“on the fly DFT”) Simulations
- Incidence conditions: $E_i = 5 \text{ eV}$ and $\vartheta_i = 15^\circ$ (w. r. t. normal incidence)
- Duration of all trajectories is $\sim 25 \text{ fs}$
- Work from Dan Auerbach, MPIbc and Geert-Jan Kroes, Uni Leiden

A special assumption in Direct dynamics

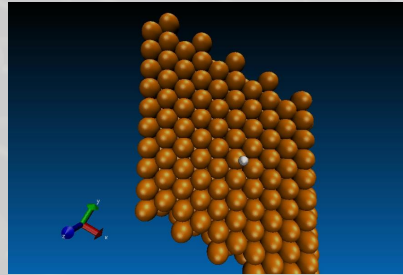
- Since Direct Dynamics calculations are so heavy, they are done on small cells (2x2x4 is typical) using periodic boundary conditions
- This means that one is simultaneously simulating large numbers of adsorption events in many neighboring cells.
- When the motion in one cell begins to influence the motion in neighboring cells, the simulation is no longer realistic.
- For H atom adsorption, it is even possible that two H atoms could encounter one another.
- Hence there is a cut-off time for Direct Dynamics. For H on Gold this cutoff time is about 100 fs.

Direct Dynamics applied to H-atom Adsorption on Au(111): Fly through

On the fly DFT for classical MD*



„Fly through“



Is it science or science fiction?

- Ab initio Molecular Dynamics (“on the fly DFT”) Simulations
- Incidence conditions: $E_i = 5 \text{ eV}$ and $\vartheta_i = 15^\circ$ (w. r. t. normal incidence)
- Duration of all trajectories is $\sim 25 \text{ fs}$
- Work from **Dan Auerbach, MPIbpc and Geert-Jan Kroes, Uni Leiden**

MPS EPFL 2013

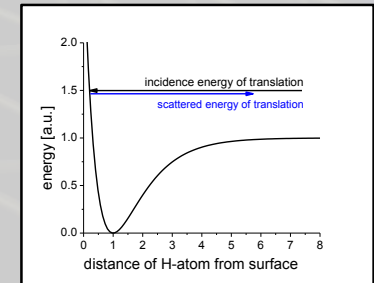
Experimental approach to understanding the adsorption at a metal surface

- Adsorption relies on translational inelasticity

- Direct measurements of translational inelasticity are needed

How:

- Photolytic H atom beam sources
- Rydberg atom tagging time-of-flight



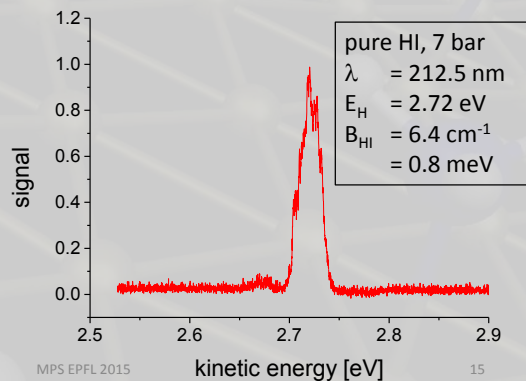
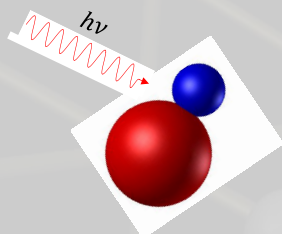
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Photolytic H-atom source

Photolysis of Hydrogen-Iodide (HI)

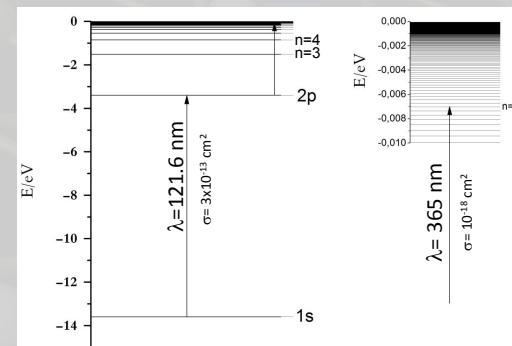
- HI cooled in a molecular beam to 5 K (removes HI internal energy)
- Dissociation of HI using monochromatic light (400 and 120 nm)
- Kinetic energy of H-atoms: 0.2eV - 7eV
- Energy width < 20 meV
- $\sim 10^7$ atoms per pulse
- In a 5-mm spot



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Rydberg Atom Tagging



ADVANTAGES

Lifetime of high Rydberg states is many μs , survives flight time to detector

Detection by field ionization + MCP is easy

TOF method applicable

No influence of space charge or stray fields

Very high resolution with high sensitivity

Background free

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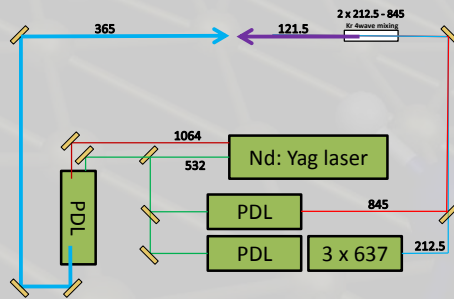
16

Laser set-up for H-atom Rydberg Tagging

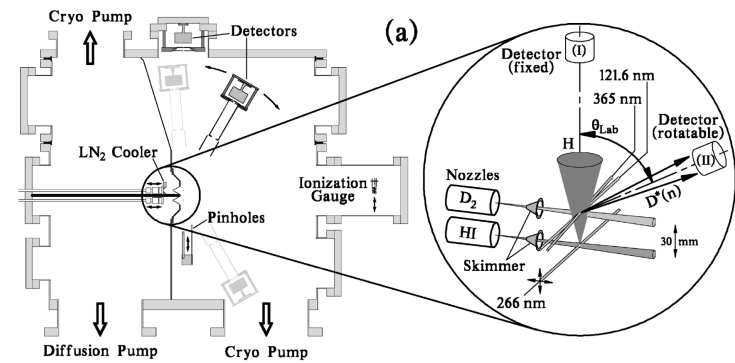
All this to generate a pulse of 121.5 nm and one of 365 nm

Legend

1. PDL - pulsed dye laser
2. Nd:Yag – Nd doped Yttrium Aluminum Garnet



All PDLs pumped by 532 (Yag green) – much more reliable



Karl Welge



Yang Xueming

Rydberg atom tagging in crossed beam reactive scattering

Schnieder, L., K. SeekampRahn, E. Wrede, and K.H. Welge, *Experimental determination of quantum state resolved differential cross sections for the hydrogen exchange reaction $H+D_2 \rightarrow HD+D$* . *J Chem Phys*, 1997. **107(16)**: p. 6175-6195.

$H+o-D_2 \rightarrow HD + D$ Results from Karl Welge's lab

- High Resolution TOF measurements of D atoms reveal the individual ro-vibrational states of HD appearing in the reaction.
- To understand this consider Energy Conservation

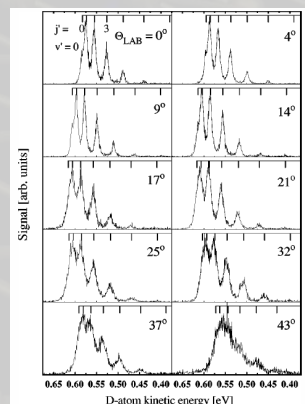
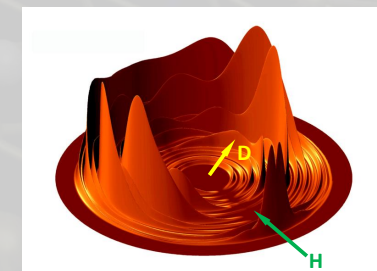
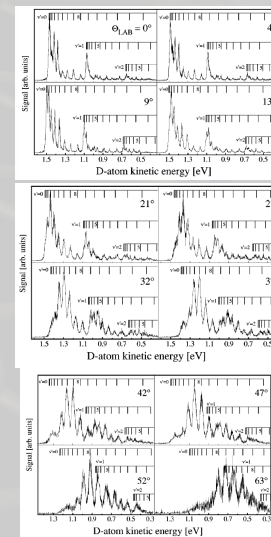


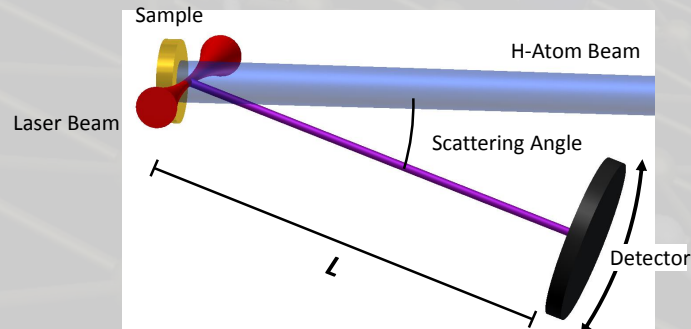
FIG. 4. D-atom LAB kinetic energy spectra recorded for $H+o-D_2 \rightarrow HD$ ($v=0$) + D at $E_{\text{cm}}=0.53$ eV.

Typical TOF data from Rydberg atom tagging



Fully rotationally resolved differential scattering cross sections

Time of flight concept

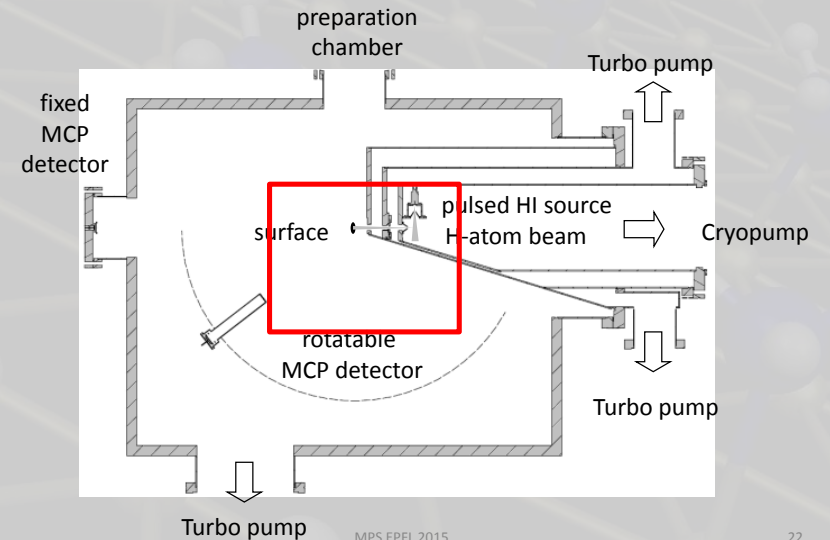


- Measure time t the atom needs to travel a known distance L .

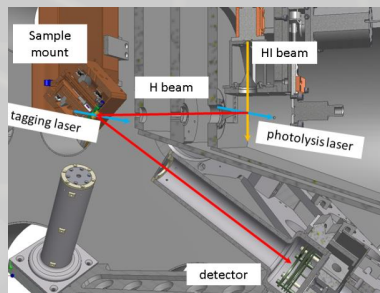
$$E_{kin} = \frac{1}{2}mv^2 = \frac{1}{2}m\frac{L^2}{t^2}$$

- To achieve high resolution L/dL and T/dt have to be large.

UHV Surface Scattering Machine

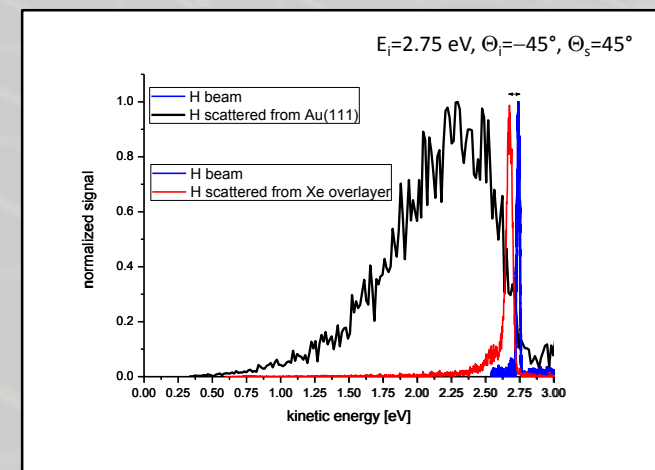


Testing the provisional model for adsorption: Rydberg atom tagging applied to H atom surface scattering



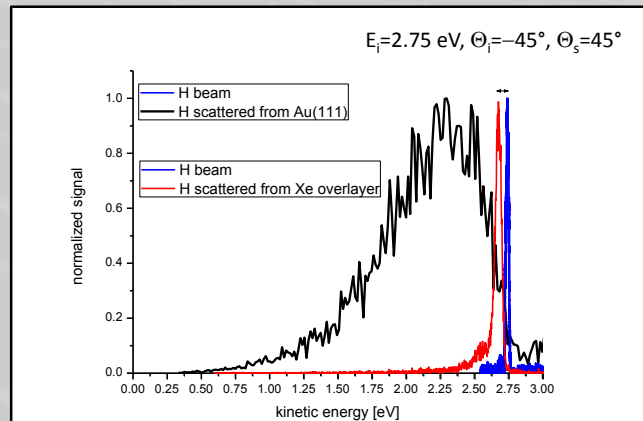
- Photolytic H-atom source from HI
- UHV compatible Rydberg tagging
- Clean single crystal Au(111)
- 25.6 cm flight distance
- 0.02 cm uncertainty in flight distance
- +/- 2.5° angular resolution

Comparing energy loss on metals and insulators



$$E' = (m_1 - m_2)^2 / (m_1 + m_2)^2$$

Comparing energy loss on metals and insulators



Born-Oppenheimer failure in H-atom collisions with a Metal

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Treating the adsorption problem theoretically

- **Option 1: Direct Dynamics**

- Heavy calculation; 1000 trajectories = 1 month

- Calculation of the potential energy surface (PES) for molecule interactions at metal surfaces is a heavy task because there are two major problems

1) (too) many degrees of freedom
and
2) Born-Oppenheimer breakdown

- Adsorption takes place on ps time-scale and involves 100's of atoms of the solid

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The Traditional Dynamical Approach applied to the adsorption problem

- The potential energy surface is constructed within the Born Oppenheimer Approximation
- Analytic functions for energies and gradients are derived by a fit to *ab initio* electronic structure data
- Classical Mechanics is employed for dynamics
- Models of electronic nonadiabaticity can be introduced
- Mixed quantum classical approaches will be used (p.s. This is tough with direct dynamics).

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A full-dimensional PES based on Effective Medium Theory

- First produce hundreds of DFT calculations including data from AIMD trajectories
- DFT data is fit with Effective Medium Theory (EMT)
- EMT gives a full dimensional PES including all Au-Au interactions. The PES describes H at the surface and in sub-surface locations.
- EMT also gives „background“ electron density needed for electronic friction calculations
- Efficient Molecular Dynamics code allows calculations up to nanoseconds duration with 1000's of atoms



Dr. Sascha Kandratsenka



Ms. Svenja Janke

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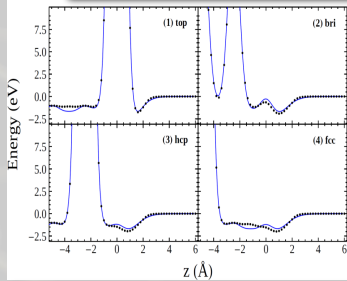
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Effective Medium Theory constrained by DFT

Au fixed at equilibrium lattice sites

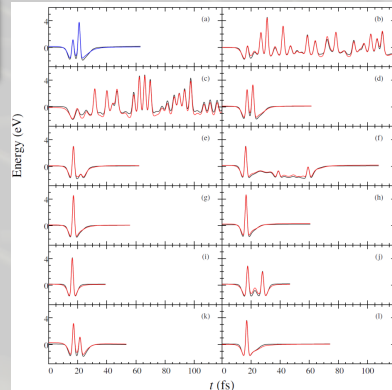
Au moving in 12 ab initio MD trajectories

A single AIMD trajectory used in the fitting



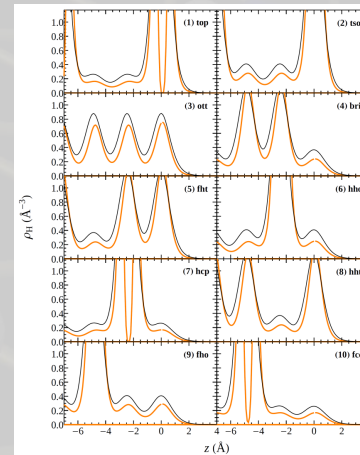
EMT also gives accurate macroscopic quantities

rms error to fit 0.14 eV



Other AIMD trajectories accurately reproduced

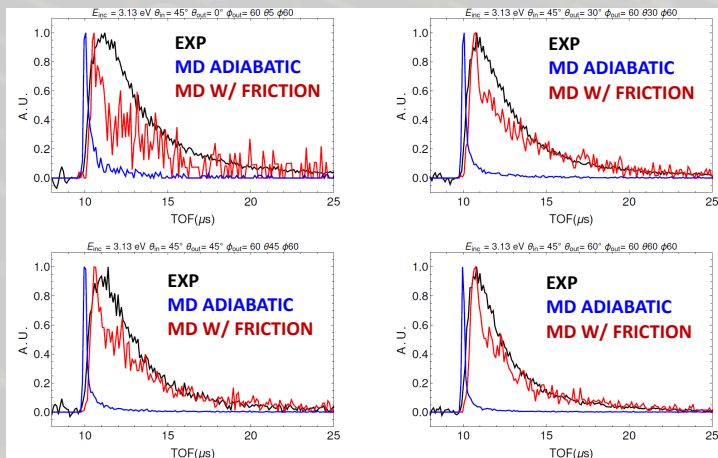
„Background“ Electron Density obtained from EMT compared to DFT densities



- **DFT vs. EMT**
- Born-Oppenheimer failure is treated as frictional effect arising from electronic excitation by nuclear motion.
- Local density electron friction approximation
 - J. I. Juaristi, M. Alducin, R. Díez Muiño, H. F. Busnengo, and A. Salin, Phys. Rev. Lett. 100, 116102 (2008).

Comparison of Experiment and theory

$E_{inc} = 3.13 \text{ eV}$, $\Theta_{inc} = 45^\circ$ Outgoing scattering angle varied

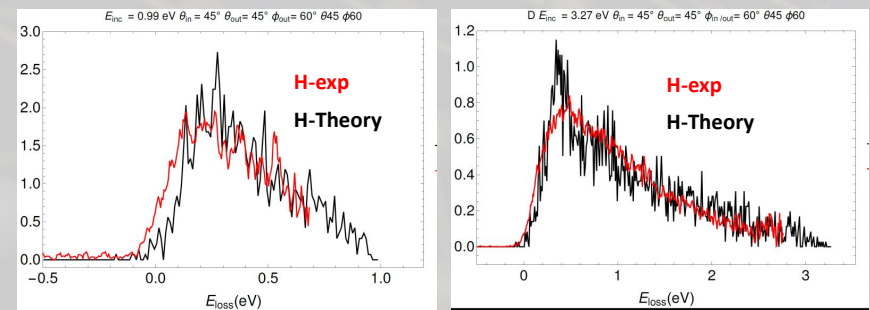


Comparison of Experiment and theory

Incidence Energy dependence

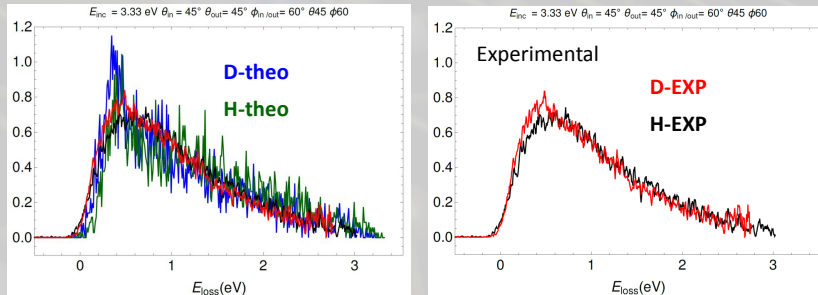
$E_{inc} = 0.99 \text{ eV}$, $\Theta_{inc} = 45^\circ$, $\Theta_{out} = 45^\circ$

$E_{inc} = 3.27 \text{ eV}$, $\Theta_{inc} = 45^\circ$, $\Theta_{out} = 45^\circ$



Comparison of Experiment and theory Isotope effect

$$E_{\text{inc}} = 3.3 \text{ eV}, \Theta_{\text{inc}} = 45^\circ, \Theta_{\text{out}} = 45^\circ$$



EMT with LDFA does a reasonable job

Experimentally observed Isotope effect is small

EMT-LDFA

An experimentally validated electronically nonadiabatic model of H-atom adsorption at a metal treated in full dimensions with hundreds of participating atoms

Born Oppenheimer Breakdown enhances sticking (Analysis of Trajectory Outcomes)

TABLE IV. Probabilities (in %) for various outcomes resulting from H-atom collisions with a Au(111) surface after 1 ps for the adiabatic and nonadiabatic simulations for two assumed electron densities (see text).

	scattering	surface adsorption	subsurface absorption	transmission
adiabatic	76	5	6	13
LDFA	47	29	22	3
LDFA scaled	50	25	21	4

Born Oppenheimer Breakdown controls dynamics (Analysis of Trajectory Outcomes)

TABLE V. Probabilities of nonadiabatic trapping pathways in % of non-scattered trajectories resolved according to the deepest penetration and final position of the H-atom. Roman numerals denote the sub-surface depth. Adiabatic results are shown in parentheses for comparison.

final	Deepest penetration					Total
surf	surf	I	II	III	>III	
surf	9 (0)	32 (2)	12 (9)	1 (9)	0 (0)	54 (19)
I		6 (0)	5 (3)	1 (3)	0 (0)	12 (6)
II			14 (3)	8 (9)	0 (1)	22 (13)
III				6 (4)	0 (1)	6 (5)
>III					6 (55)	6 (55)

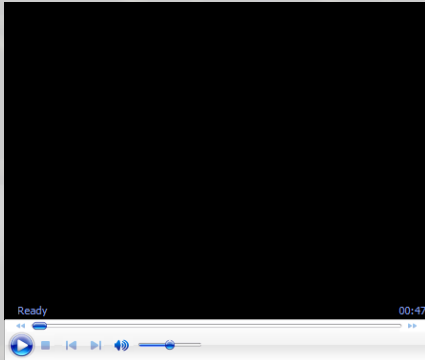
○ Penetration Re-surfacing

○ Surface Skidding

Tuning up the world's greatest microscope

- Many ps long full-dimensional simulations of adsorption including effects of electronic excitation

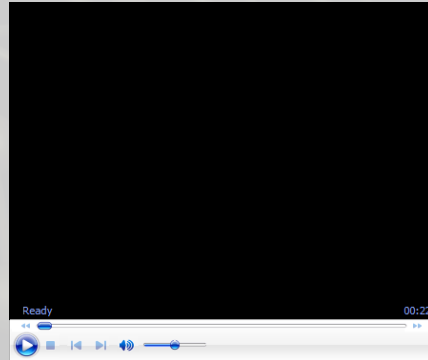
Penetration/re-surfacing



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Surface skidding

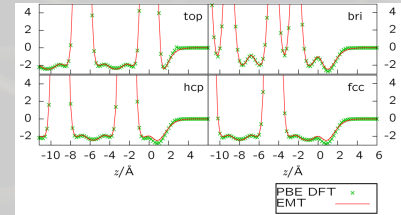


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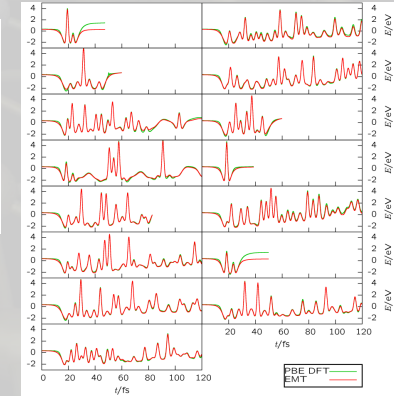
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New PES produced in two months H – Pd PES

Fcc lattice positions



AIMD trajectories



Master's thesis of Mr.
Marvin Kammler

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EMT offers a „supercharged“ form of AIMD

- Effective medium Theory provides analytic functions that yield the full dimensional atomic forces and electron density distributions with the accuracy of DFT-GGA.
- It forms the basis for more sophisticated treatments of the dynamics including:
 - Building and testing new models of Born-Oppenheimer breakdown
 - Quantum dynamics
- Can now be easily computed for H atom interactions with many solids

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Summary and Conclusions

- I showed you a full dimensional trajectory simulation of H adsorption at a metal surface involving hundreds of atoms moving for several picoseconds.
- The Dominant energy loss occurs to electron hole pairs and controls the adsorption probability and dynamics
- “Penetration re-surfacing” and “surface skidding” are the most important adsorption mechanisms
- The simulations are based on a full dimensional global PES of the effective medium theory that has been fitted to DFT points where all atoms move
- Phonon and electron hole pair excitation are treated self consistently at the level of local density friction approximation
- These results have been validated against H atom scattering experiments showing electron-hole pair excitation dominates the translational inelasticity

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Measuring Accurate Thermal Rates of Surface Chemical Reactions

New tools for old problems

Thermal Reaction Rates at Surfaces

- The goal of chemical dynamics is to develop predictive theoretical capability via fruitful collaboration with experiment for describing the precise atomic motion taking place during chemical reactions. Of course, such capability can predict reaction rates.
- Measuring surface chemical reaction rates is difficult. Just as we needed comparisons of experiment and theory for H atom scattering from Au(111), we will need comparisons of theoretical predictions of reaction rates to accurate experimental results
- It is important then to develop new measurement tools for simple problems like: What is the rate of a chemical reaction?

Velocity-resolved residence-time measurements

CO desorption from Pt(111)

- A prototypical surface rate process, well suited to testing new experimental methods
- Many previous measurements have been made, exemplifying the difficulty of measuring accurate rates in surface chemistry
- Desorption rates can yield accurate binding energies – CO/Pt(111) binding has been a testing ground for state of the art theory

CO – Pt(111) Binding energy

- Desorption Rates can lead to accurate binding energies

– TST expression for desorption rate

$$k_{des}(T_S) = s(T_S) \frac{k_B T_S}{h} \frac{Q^\ddagger}{Q_{ads}} e^{-E_0/k_B T_S}$$

$s(T_S) \equiv$ Thermal sticking coefficient (transition state re-crossing correction)

$Q^\ddagger \equiv$ partition function of the TS

$Q_{ads} \equiv$ partition function of the reactant

$E_0 \equiv$ barrier to desorption - if no barrier to adsorption \equiv binding energy

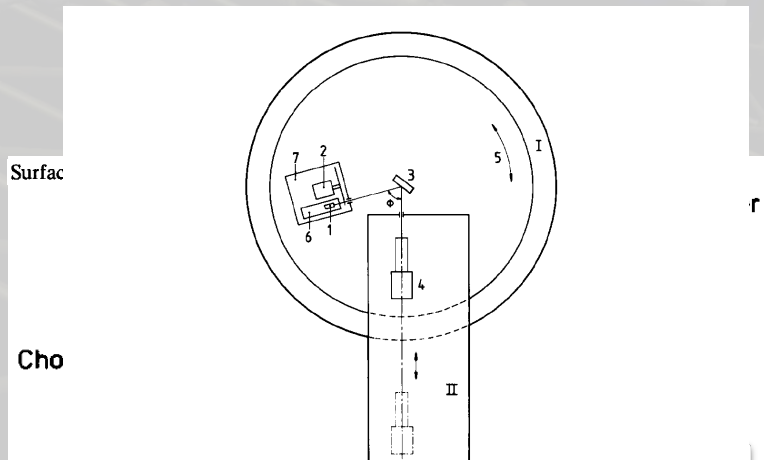
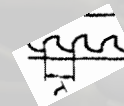


Fig. 1. Scheme of the apparatus. The angle ϕ between the molecular beam and the detector axes can be varied between 40° and 185° by rotating the disk (5) on which the nozzle (1), the chopper (2) and differential pumping stages (6 and 7) are mounted. The sample (3) is located in the center of the main chamber (I). The movable detector (4) is located inside the detector chamber (II).

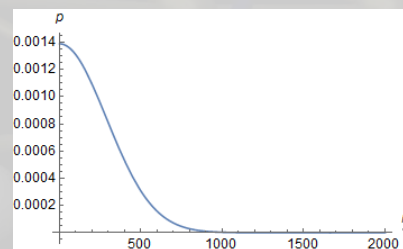
Laurens J and Geot

The time dependence of the signal: Two effects

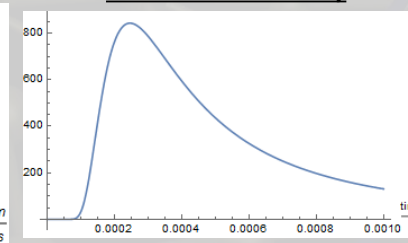


Time dependence, of course, depends on the residence time

1D Maxwell Boltzmann distribution $T=300K$

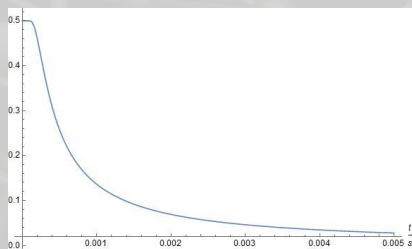


Arrival time distribution at a detector 10 cm away



↑
250 microsecond

Convolution of a step function over the time of arrival function



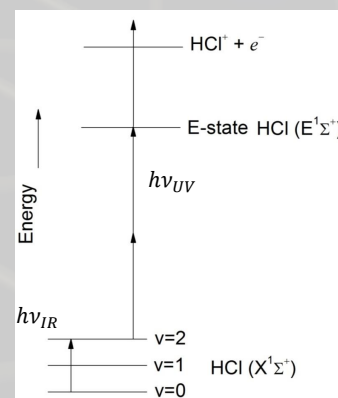
This time dependence looks startlingly like a residence time would look. It defines the time response of the experiment, making it much worse.

We need to be able to distinguish the residence time from the flight time to the detector

We need residence time measurements of molecules desorbing with a selected velocity

IR-UV double resonance: Principle of state-to-state TOF

Energy Diagram

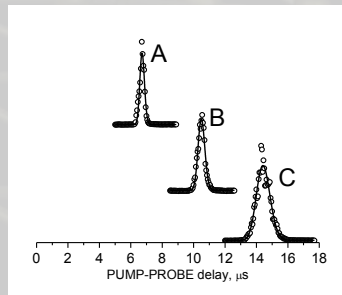
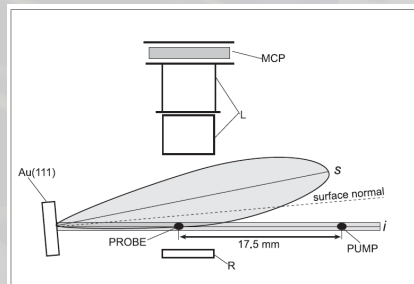


Energy balance

- Initial state determined by the IR laser
- The final state is determined by the UV laser
- E_i determined by molecular beam
- E_f determined by measured TOF

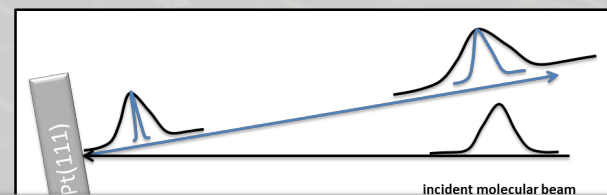
IR tagging of HCl($v=0$) in a beam velocity measurement

Pump HCl($v=0, J=0$) to $v=2, J=1$ with IR pulse
 Probe HCl($v=2, J=1$) with REMPI



- (A) 1% HCl/H₂ with $E_i = 1.27$ eV;
- (B) 10% HCl/H₂ with $E_i = 0.52$ eV;
- (C) 10% HCl/20% N₂/70% D₂ with $E_i = 0.28$ eV.

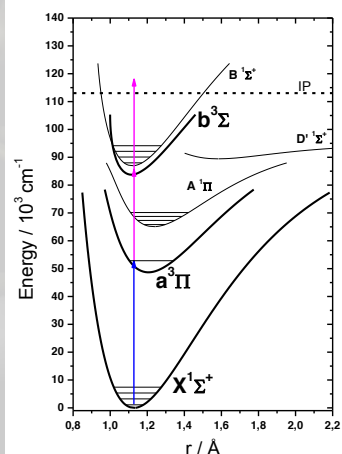
Velocity-resolved residence times



A two dimensional TOF measurement is possible.

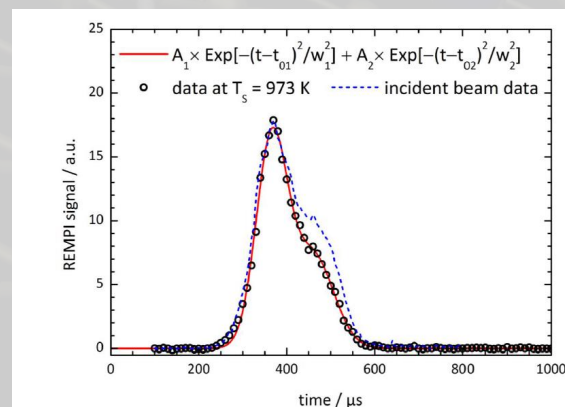
The delay between the two laser pulses defines the velocity of the desorbing molecules, while the timing of the pulsed molecular beam can be used to obtain the residence time

Electronic spectroscopy of CO



- Two important bands
 - $a^3\Pi_1(v=0) \leftarrow X^1\Sigma^+(v=0)$
 - $a^3\Pi_1$ millisecond lifetime
 - Used to tag desorbing CO molecules
 - $b^3\Sigma^+(v=0) \leftarrow a^3\Pi_1(v=0)$
 - 1+1 REMPI
 - To selectively detect the tagged CO molecules

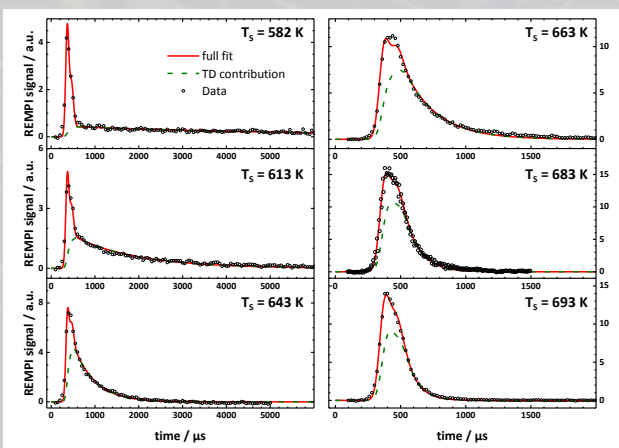
The CO-dosing molecular beam pulse



Velocity selected residence time measurement in high T_s limit

Fit to two Gaussians and used in the fitting

Velocity resolved residence time vs T_s

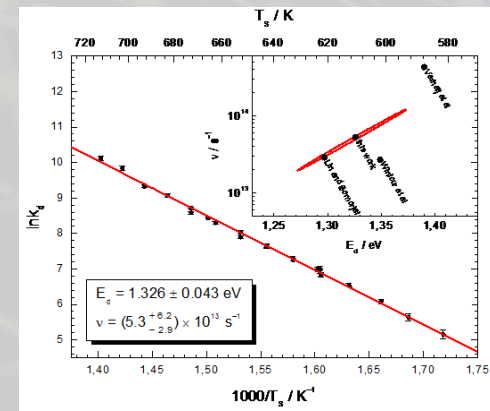


With a defined CO velocity, the data represent desorbing flux.
Not only are random errors in this measurement small, systematic errors associated with the CO velocity distribution are removed

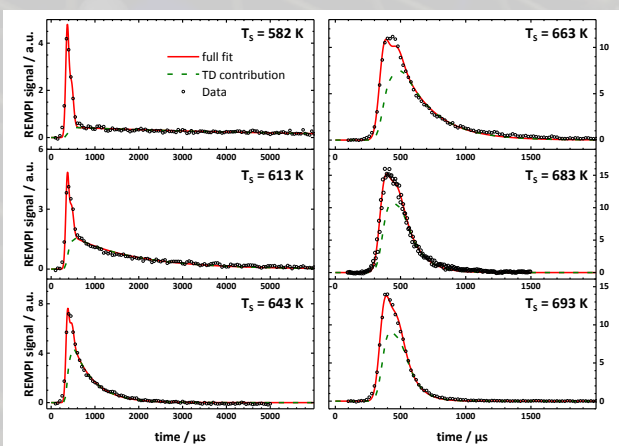
1st-order rate constants derived

- Comparison to previous work

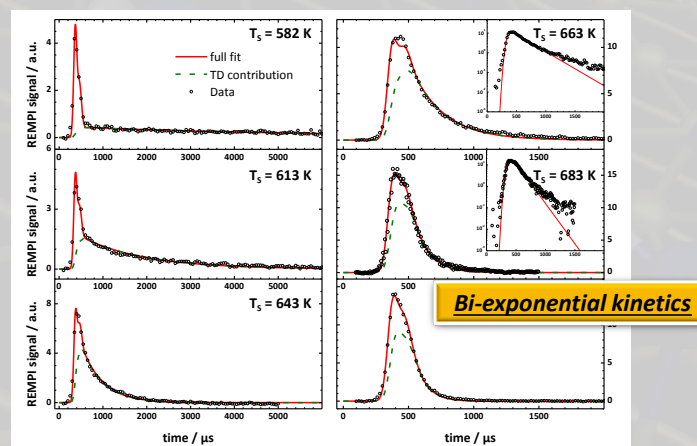
E_d / eV	ν / s ⁻¹	Reference
1.321	$(4.7^{+4.9}_{-2.4}) \times 10^{13}$	This work
1.297	2.9×10^{13}	Lin
1.349	2.7×10^{13}	Winicur
1.39	4.3×10^{14}	Verheij
1.51	1.25×10^{15}	Campbell



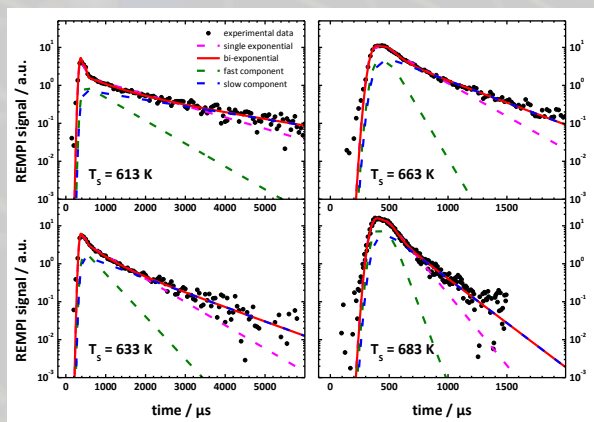
Velocity resolved residence time vs T_s



Velocity resolved residence time vs T_s



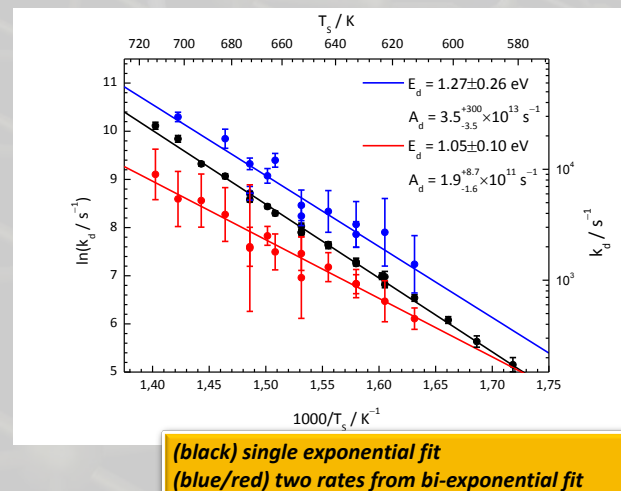
Bi-exponential kinetics of CO desorption from Pt(111)



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Two rate processes



(black) single exponential fit
(blue/red) two rates from bi-exponential fit

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Explanation of bi-exponential kinetics

- Step density 1% ML $\sim 3 \times 10^{13} \text{ cm}^{-2}$
- Molecular beam Dose 3% ML $\sim 1 \times 10^{14} \text{ cm}^{-2}$
- Under these conditions: CO dosing saturates step sites – diffusion is fast – leaving similar populations at terraces and steps.
- Desorption follows by two processes.
 - Desorption from terraces
 - Diffusion from steps to terraces then desorption

The influence of steps on the desorption kinetics of NO from Pt(111)

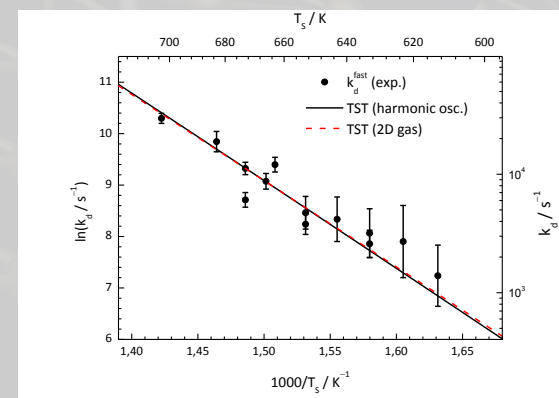
J. A. Serri, J. C. Tully, and M. J. Cardillo

J. Chem. Phys. 79(3), 1 Aug. 1983 1530

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Modeling terrace desorption with transition state theory



$$k_{des}(T_S) = S(T_S) \frac{k_B T_S}{h} \frac{Q^\ddagger}{Q_{ads}} e^{-D_0/k_B T_S}$$

$D_0 = 1.47 \pm 0.04 \text{ eV}$ ($34 \pm 1 \text{ kcal/mole}$).

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CO binding to Pt(111) is a puzzle

The CO/Pt(111) Puzzle[†]

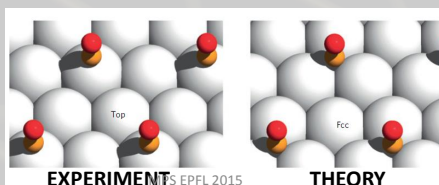
J. Phys. Chem. B **2001**, *105*, 4018–4025

Peter J. Feibelman,^{*,‡} B. Hammer,[§] J. K. Nørskov,[¶] F. Wagner,[‡] M. Scheffler,[‡] R. Stumpf,[¶] R. Watwe,[¶] and J. Dumesic[¶]

Sandia National Laboratories, Albuquerque, New Mexico 87185-1413, Institute of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark, Center for Atomic-Scale Materials Physics, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany, Motorola Corporation, Computational Materials Group, Sandia National Laboratories, Albuquerque, New Mexico 87185-1415, and Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

Received: June 27, 2000; In Final Form: August 22, 2000

Notwithstanding half a dozen theoretical publications, well-converged density-functional calculations, whether based on a local-density or generalized-gradient exchange-correlation potential, whether all-electron or employing pseudopotentials, underestimate CO's preference for low-coordination binding sites on Pt(111) and vicinals to it. For example, they imply that CO should prefer hollow- to atop-site adsorption on Pt(111), in apparent contradiction to a host of low-temperature experimental studies.



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Random Phase Approximation

PHYSICAL REVIEW B **80**, 045402 (2009)

Exploring the random phase approximation: Application to CO adsorbed on Cu(111)

Xinguo Ren,^{1,*} Patrick Rinke,^{1,2} and Matthias Scheffler^{1,2,3}

¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

²Materials Department, University of California, Santa Barbara, California 93106, USA

³Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, USA (Received 19 March 2009; revised manuscript received 7 June 2009; published 2 July 2009)

The adsorption of CO on the Cu(111) surface is investigated in the random phase approximation (RPA) as formulated within the adiabatic connection fluctuation-dissipation theorem. The RPA adsorption energy is obtained by adding a "local exchange-correlation correction" that is extrapolated from cluster calculations of increasing size, to the Perdew-Burke-Ernzerhof (PBE) value for the extended system. In comparison to density-functional theory calculations with the generalized gradient functionals PBE and AM05 and the hybrid functionals PBE0 and HSE03, we find a hierarchy of improved performance from AM05/PBE to PBE0/HSE03, and from PBE0/HSE03 to RPA, both in terms of the absolute adsorption energy as well as the adsorption-energy difference between the atop and the hollow fcc sites. In particular, the very weak atop site preference at the PBE0/HSE03 level is further stabilized by about 0.2 eV in the RPA. The mechanism behind this improvement is analyzed in terms of the *GW* density of states that gives a spectral representation in par with the RPA formalism for the total energy.

DOI: 10.1103/PhysRevB.80.045402

PACS number(s): 68.43.Bc, 71.15.Mb, 68.47.De

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nature
materials

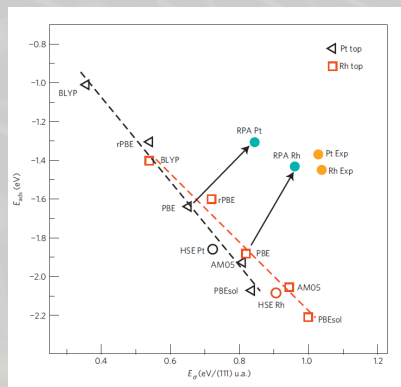
LETTERS

PUBLISHED ONLINE: 25 JULY 2010 | DOI: 10.1038/NMAT2806

Accurate surface and adsorption energies from many-body perturbation theory

L. Schimka^{1,*}, J. Harl¹, A. Stroppa^{2,†}, A. Grüneis¹, M. Marsman¹, F. Mittendorfer¹ and G. Kresse¹

Kohn-Sham density functional theory is the workhorse computational method in materials and surface science¹. Unfortunately, most semilocal density functionals predict surfaces to be more stable than they are experimentally. Naively, we would expect that consequently adsorption energies on surfaces are too small as well, but the contrary is often found: chemisorption energies are usually overestimated². Modifying the functional improves either the adsorption energy or the surface energy but always worsens the other aspect. This suggests that semilocal density functionals possess a fundamental flaw that is difficult to cure, and alternative methods are urgently needed. Here we show that a computationally fairly efficient many-electron approach, the random phase approximation³ to the correlation energy, resolves this dilemma and yields at the same time excellent lattice constants, surface energies and adsorption energies for carbon monoxide and benzene on transition-metal surfaces.

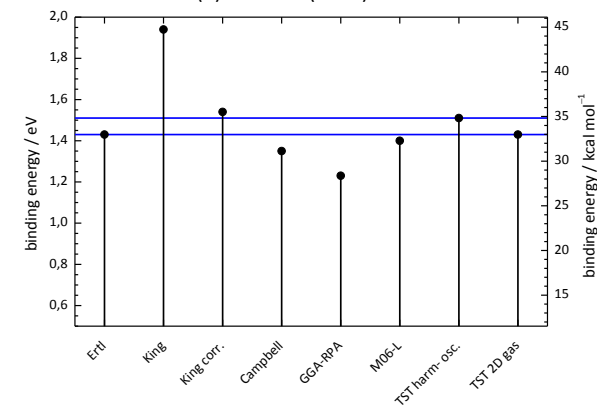


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Comparison with previous work

J. Am. Chem. Soc. **137**(4) 1465-75 (2015)

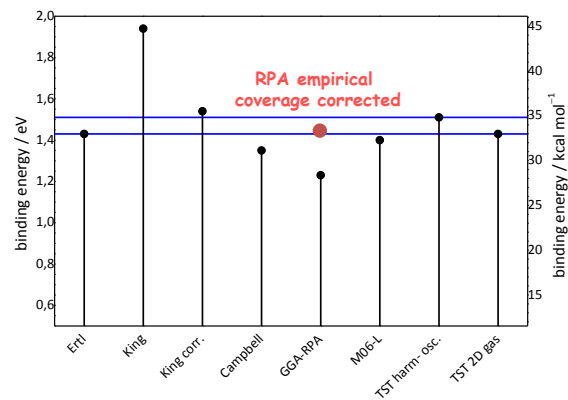


GGA-RPA still has large (6 kcal/mole) error
GGA with one of the Minnesota functionals gives close agreement

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A note about the accuracy of RPA

- RPA
- The
- The
- Ex de 15



Summary and Conclusions

- We investigated CO desorption from Pt(111) for a crystal with 0.5-1% ML step density
- We implemented a double resonance method allowing measurement of velocity selected residence times.
- We dosed Pt pulses delivering 3% ML, revealing bi-exponential kinetics involving two mechanisms
 - Desorption from terraces and
 - Sequential step-to-terrace diffusion followed by desorption
- We modelled the bi-exponential kinetics with a microscopic model involving diffusion to steps – in this way we identified the terrace desorption process.
- We derived the CO binding energy using TST – it is in good agreement with previous experiments
- It appears that DFT-RPA gives a good binding energy for CO binding at Pt(111) if we estimate the CO-CO repulsive forces.

Adsorption relies on Born-Oppenheimer breakdown



without electron excitation,
Scattering is favored



with electron excitation adsorption is
enhanced: penetration/re-surfacing

Generation of short H-Atom Pulses

Perspectives for pump-probe
experiments using pulses of matter

Generation of ultra-short Hydrogen atom pulses by bunch-compression photolysis, Sven Kaufmann, Dirk Schwarzer, Christian Reichardt, Alec M. Wodtke, Oliver Bünermann, [Nature Communications](https://doi.org/10.1038/ncomms6373), DOI:10.1038/ncomms6373 (2014)

Short pulses of neutral matter versus short pulses of light

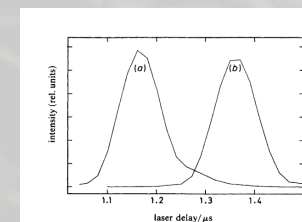
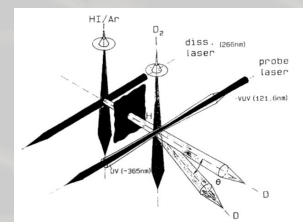
- **Molecules are slow, light is fast**
 - v_{molecule} typically $<10^{-5} c$
 - For molecules, production and detection volumes must be kept small, $v=10 \text{ km/s}$ then $1 \mu\text{m}$ is 100 ps
 - For light $1 \mu\text{m}$ is 3 fs
- **Molecules have speed distributions, light travels with a single speed (e.g. in vacuum)**
 - Short pulses of molecules spread
 - Short pulses of light stay together

H-atom pulses by photolysis of HI

Faraday Discuss. Chem. Soc., 1991, 91, 259-269

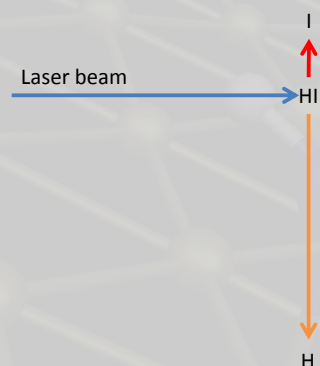
Hydrogen Exchange Reaction $\text{H} + \text{D}_2$ in Crossed Beams

L. Schnieder, K. Seekamp-Rahn, F. Liedeker, H. Steuwe and K. H. Welge*
Fakultät für Physik, Universität Bielefeld, 4800 Bielefeld 1, Germany



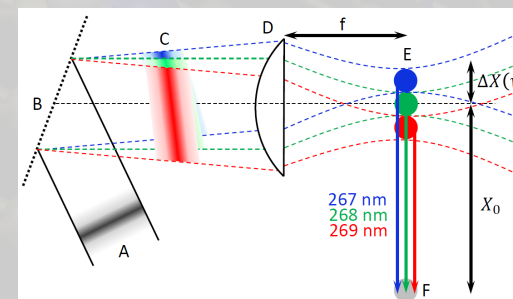
Short pulses of neutral matter- the problem

- Femto-second laser can be used to photolyze a molecule and produce a short pulse of photoproducts.
- e.g. $\text{HI} + h\nu \longrightarrow \text{H} + \text{I}$
- However,
 - fs lasers have a photon energy width. So, the neutral matter pulse will spread as it travels
 - The laser must be focussed as tightly as possible to limit flight distance uncertainty-



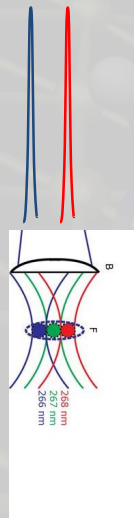
Bunch-compression photolysis - Concept

- Bunch compression takes place from an extended volume – both problems solved simultaneously.



The input laser beam (A) is dispersed on a grating (B). The diverging pulse (C) is focused with lens (D) with focal length, f . The single frequency components are focused onto spots with a spatial detuning, $\Delta X(\nu)$, relative to the central frequency. This is depicted in a schematic fashion for three selected wavelengths. Due to the continuous frequency shift, these spots are not separated and yield a focal line (E). The H-atoms are generated by photodissociation at different laser frequencies and emerge with different speeds, such that the initial H-atom photo-product bunch is compressed at spot (F).

Spatial chirp leads to bunch-compression

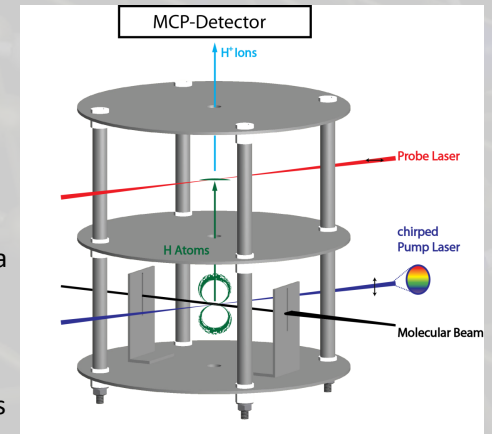


- *Photolysis of molecular beam cooled HI with a spatially chirped fs laser pulse*
 - 4th harmonic of Ti-Sapph chirped with a grating
 - Large mass of I and sampling of beam at \perp direction lead to $T_{\text{trans}} \sim 0\text{K}$
 - Rotational cooling $T_{\text{rot}} \sim 10\text{K}$

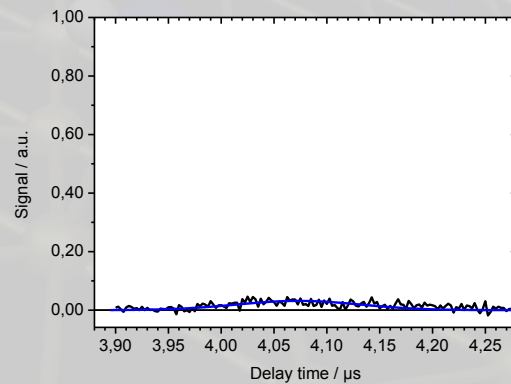
$D_{\text{re-bunch}}$

Bunch-compression photolysis - Experiment

- $v_{\text{H}} = 10.9 \text{ km/s}$
- Non-resonant MPI with focused Ti-Sapph
- Effective time resolution limited by focusing is 5 ns
- H^+ detected while scanning a delay line between PUMP and PROBE laser pulses
- Pulse picker used to introduce controlled fixed μs delay

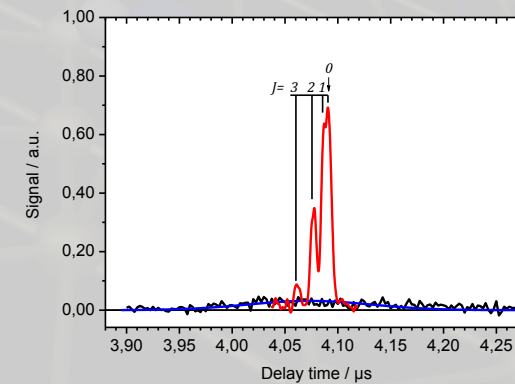


Conventional photolysis



Tightly focused 150 fs photolysis laser pulse
150 ns long pulse broadened by the laser photon energy spread

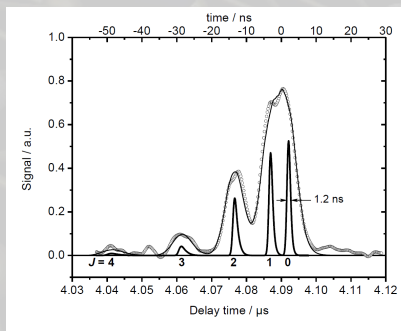
Bunch-compression photolysis



Line focused 150 fs photolysis laser pulse
Pulse train reflects the rotational states of HI populated in the beam

Bunch-compression photolysis - Realization

- We demonstrate H-atom pulses with 1.2 ± 0.3 ns duration
- Simulations indicate H-atom pulses shorter than 40 ps duration can be produced with existing lasers.
- Bunch-compression is also compatible with large (mm^3) photolysis volumes, an advantage for H-atom beam intensity.



This technique overcomes one of the most challenging impediments to a new class of experiments on time-resolved dynamics in gas-gas as well as gas-surface interactions.

MPS EPR 2013

