Vibrational coupling: most important, often ignored, and a challenge for ab-initio theory

November 6, 2012 to November 9, 2012

cecam Centre Européen de Calcul Atomique et Moléculaire

cecam-MM1P.de |Φ> multi-scale modeling from first priciples

Psi-k.org

Program - Session I: Non-adiabaticity

14:30 to 14:40	Welcome	
14:40 to 15:00	Heiko Appel	**Introduction to the session and discussion moderator**
15:00 to 15:40	Eberhard K.U. Gross	**How to make the Born-Oppenheimer approximation exact: A fresh look at potential energy surfaces and Berry phases in the time domain**
15:40 to 16:00	Discussion	
16:00 to 16:20	Coffee Break	
16:20 to 17:00	Ivano Tavernelli	**Nonadiabatic couplings and nonadiabatic dynamics within TDDFT**
17:00 to 17:20	Discussion	
17:20 to 18:00	Andrew Horsfield	**How do you build a good Hamiltonian for CEID?**
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Definition of "non-adiabatic"?

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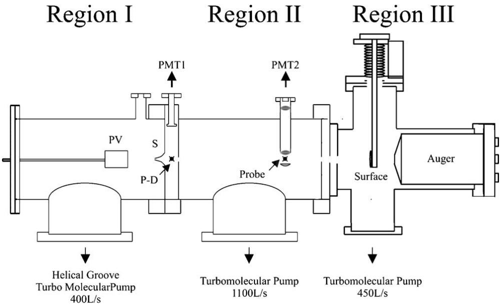
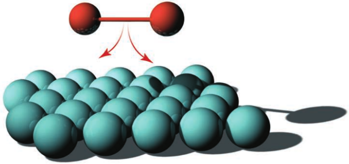
$\longrightarrow$ purely theoretical concept

In nature/experiment vibronic and vibrational coupling is always present at full stregth - cannot be switched off

NO scattering from a gold surface





Jason D. White et. al. JCP 124, 064702 (2006).

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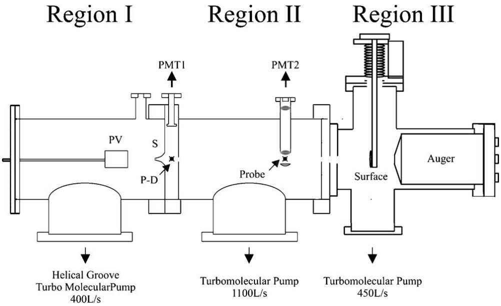

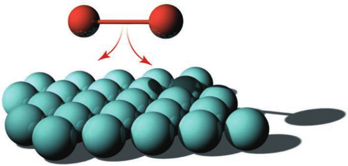

- Supersonic NO beam from pulsed valve is collimated by an electroformed skimmer S

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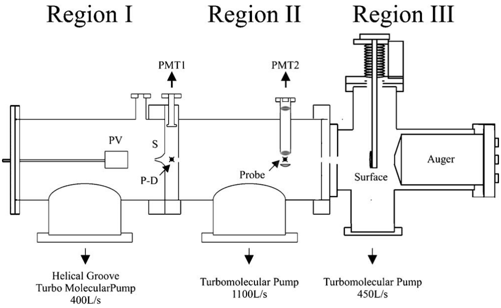

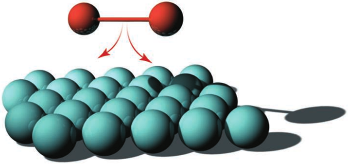

- Supersonic NO beam from pulsed valve is collimated by an electroformed skimmer S
- Two-laser optical pumping at (P-D)

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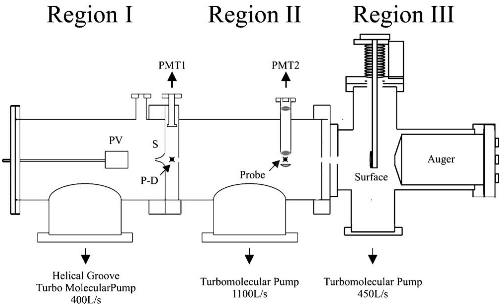

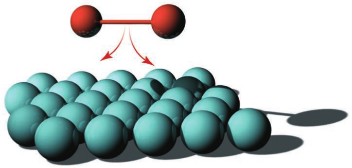

- Supersonic NO beam from pulsed valve is collimated by an electroformed skimmer S
- Two-laser optical pumping at (P-D)
- Scattering of NO beam with Cs/Au surfaces, detection of electron emission

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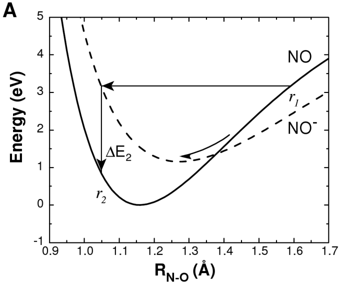
NO scattering from a gold surface - Newns-Anderson model

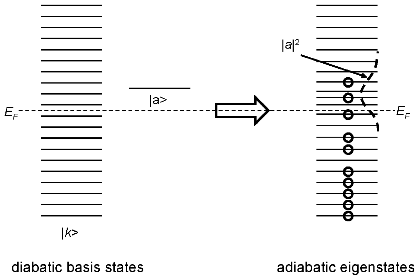
Newns-Anderson Hamiltonian

$$H_{\mathrm{el}} = U_0(\mathbf{R}) + \sum_{j=1}^{N_e} E_j(\mathbf{R}) \hat{c}_j^\dagger \hat{c}_j$$

$$H_{\mathrm{el}}^1 = [U_1(\mathbf{R}) - U_0(\mathbf{R})] \,|\, a \rangle\langle a \,| + \sum_{k=1}^{M} \varepsilon_k \,|\, k \rangle\langle k \,|$$

$$+ \sum_{k=1}^{M} [V_{ak}(\mathbf{R}) \,|\, a \rangle\langle k \,| + V_{ka}(\mathbf{R}) \,|\, k \rangle\langle a \,|]$$





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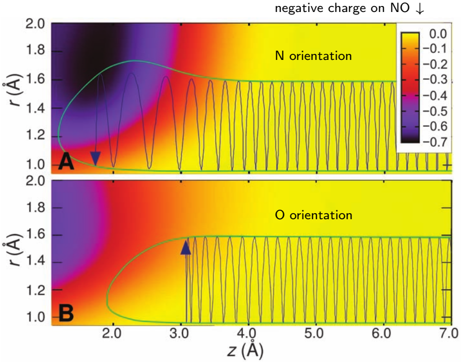

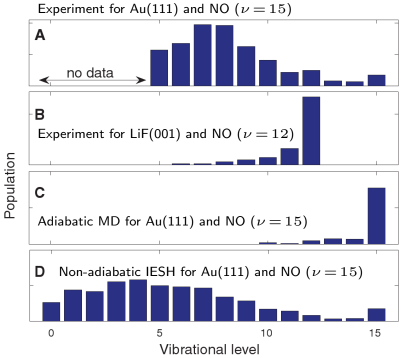

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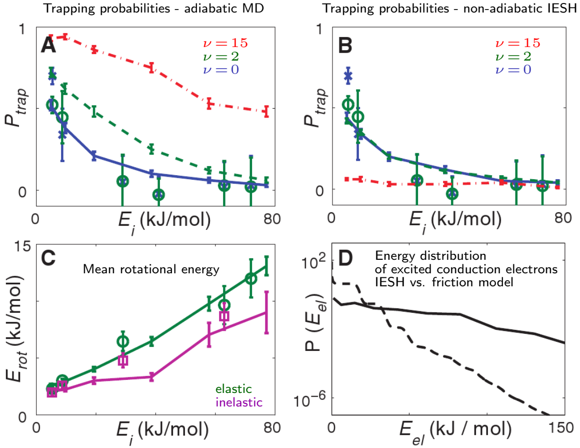

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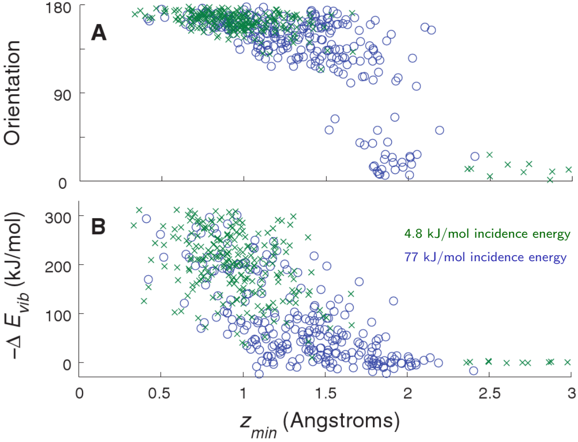

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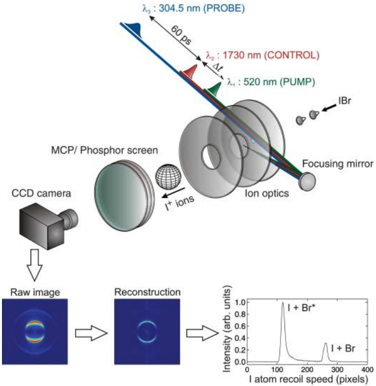
NO scattering from a gold surface

What is still missing?

- non-interacting electrons in the Newns-Anderson Hamiltonian
- no electronic thermalization in the surface after transfer of impact and vibrational energy (cf. talk of Karsten Reuter)
- difficult to extend approach if more than two molecular states play a role

Dynamical Stark Control of Photochemical Processes



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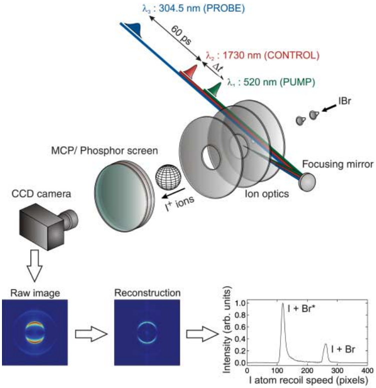

- 100fs pump pulse at 520nm
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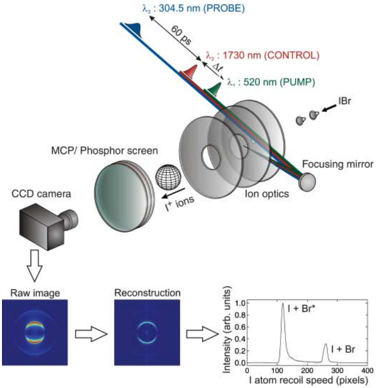

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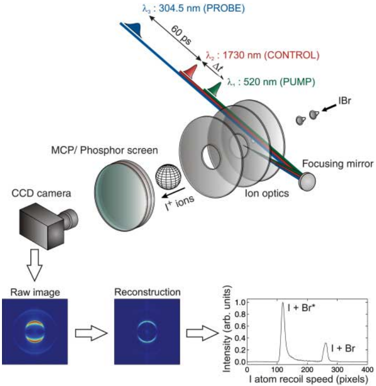

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- after 60ps probe pulse at 304.5nm
  (2+1) resonance-enhanced multi-photon ionization (REMPI) produces I^+ ions.

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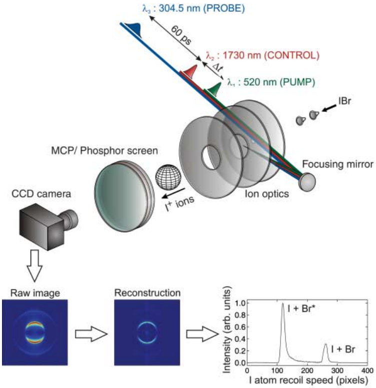

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- Field free branching ratio of Br*/Br = 3.5

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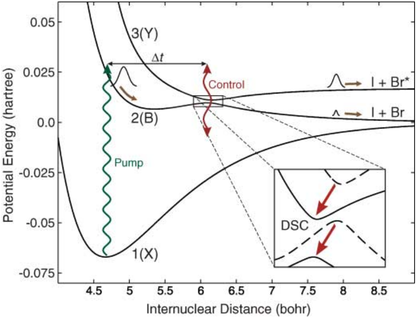

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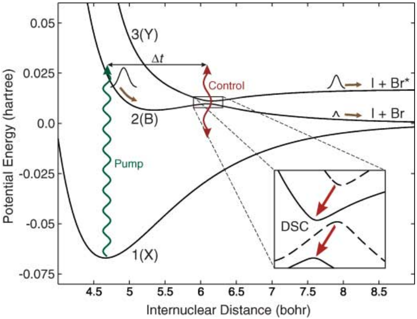

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- Landau-Zener curve-crossing probability

$$P = e^{2\pi\Gamma}, \quad \Gamma = \frac{V_{23}}{v\partial_R[V_2(R) - V_3(R)]}$$

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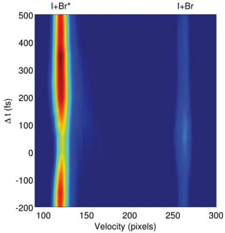

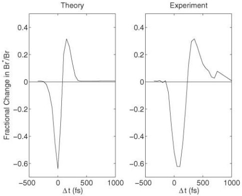

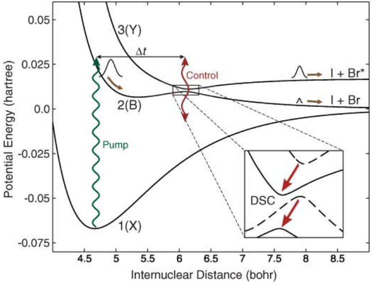

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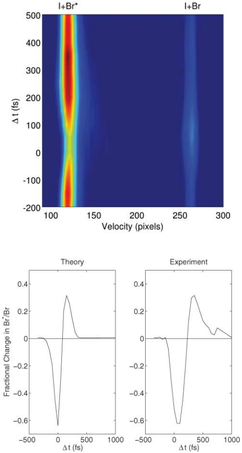

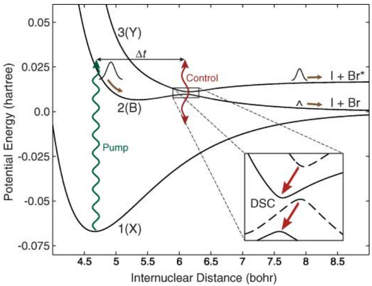

- 60% enhancement of Br yield at $\Delta t = 0$

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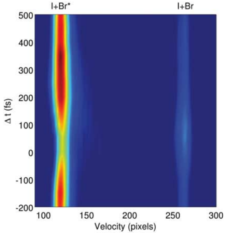

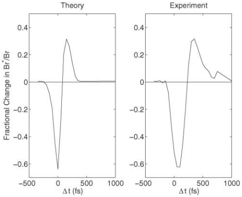

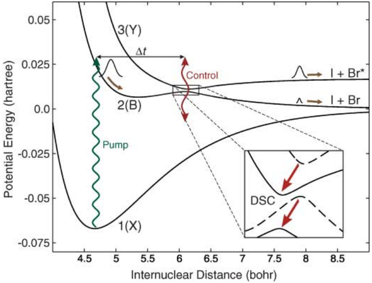

- 60% enhancement of Br yield at $\Delta t = 0$
- Br* yield enhanced by 30% at $\Delta t = 300$ (traversal of the crossing)

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Session I: Non-adiabaticity - Challenges posed by the speakers

Eberhard K.U. Gross

- tba 1
- tba 2

Ivano Tavernelli

- What methods do we have available for the calculation of el-ph couplings?
- Accuracy of DFT/TDDFT vs. GW (BSE) for the calculation ph-el couplings?

Andrew Horsfield

How do you construct a Hamiltonian matrix that

- You can compute?
- Incorporates many electron effects?
- Incorporates electron-phonon interactions?
- Is robust?
- Makes the resulting equations of motion as simple as possible?