Atomistic Understanding of Plasmon Mediated Photochemical Reactions

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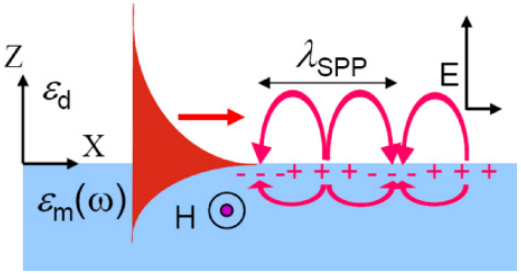
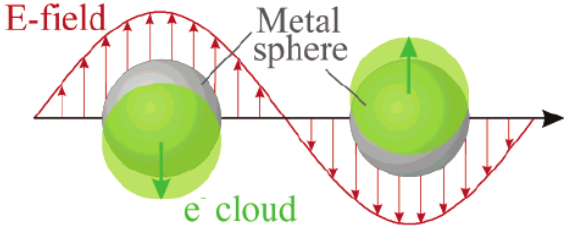
LA-UR-20-30317

Plasmonics

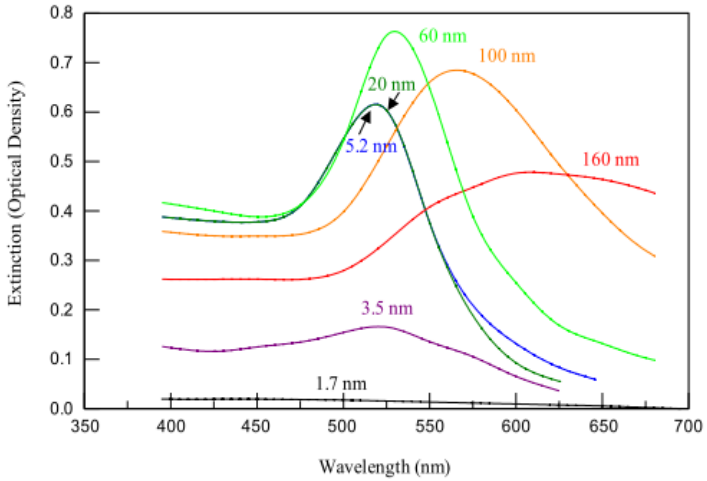
Polarization of metal surface under external electric field:



Surface Plasmon Polariton



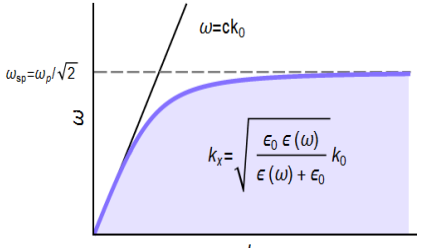
Localized Surface Plasmon

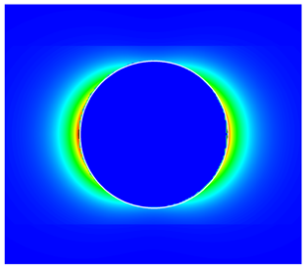


Lycurgus cup

Properties of Plasmonics:

- Short wavelengths
- Localization of field
- Enhancement



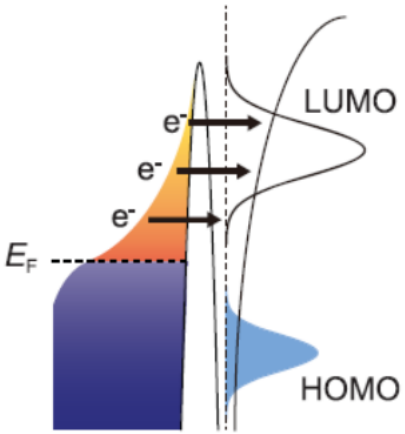


Applications:

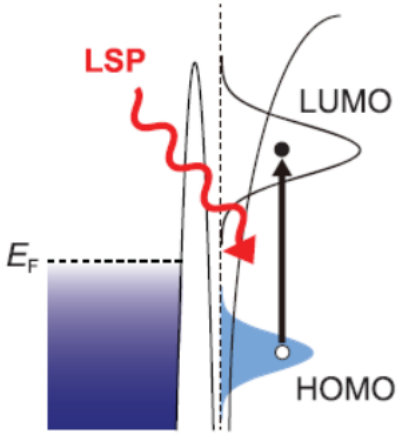
- Surface Enhanced Raman Spectroscopy
- Surface plasmon enhanced single molecule detection
- Nano assembly and patterning
- Surface plasmon enhanced photovoltaic conversion
- Plasmonic metamaterials
- ...

Plasmon-mediated Chemistry

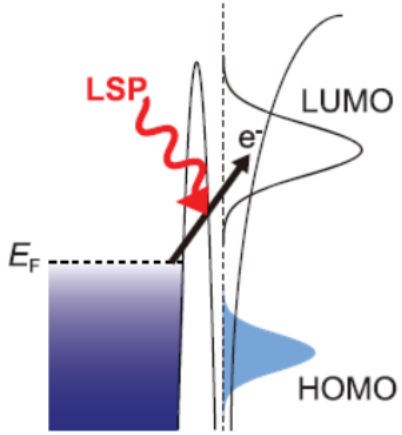
Enhance direct intramolecular excitation	Science, 526, 521 (2018), JPCC, 121, 7421 (2017), Nat. Commun. 7, 10545 (2016)
Direct charge transfer	J. Am. Chem. Soc. 134, 14238 (2012) J. Am. Chem. Soc. 136, 4343 (2014) ACS Nano, 10, 6108 (2016), Science, 349, 632 (2015)
Indirect hot-electron transfer.	Nano Lett., 13, 240(2013), Nat. Mat. **11**, 1044 (2012) Nat. Chem. 3, 467 (2011), Nano Lett., 18, 2189 (2018), …
Local heating effect	JPCC 122, 5657 (2018), JPCC 122, 5040 (2018)



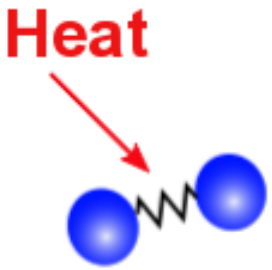
Indirect excitation



Intramolecular excitation



Direct excitation

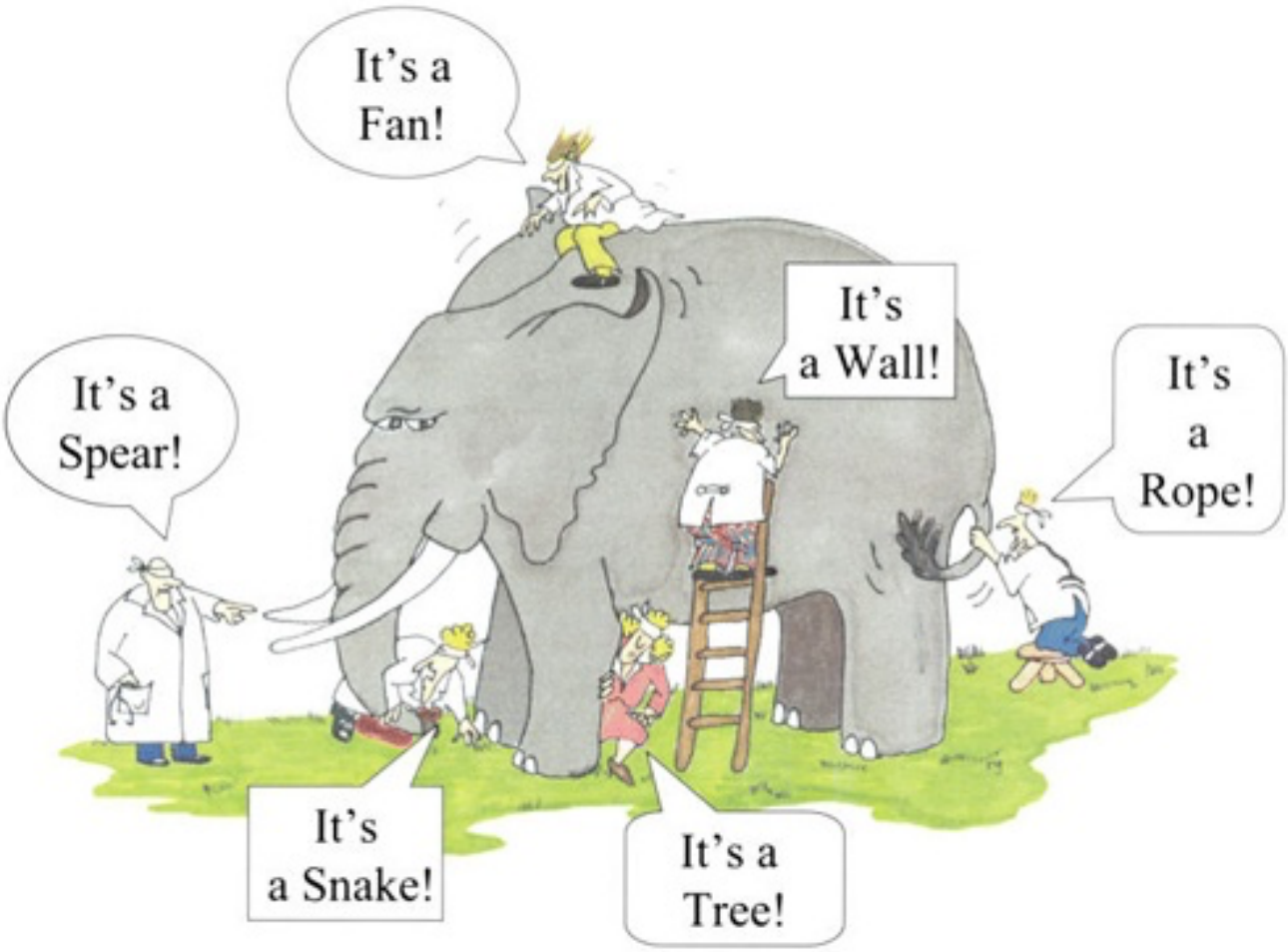


Local heating effect

Angew. Chem. Int. Ed. 58, 2 (2019)

Mechanisms of Plasmon-mediated Chemistry are unclear

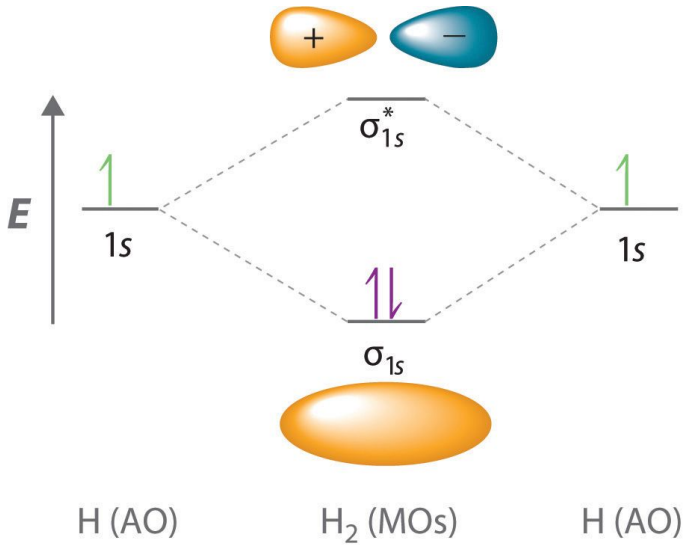
- Plasmon mediated chemistry is complicated:

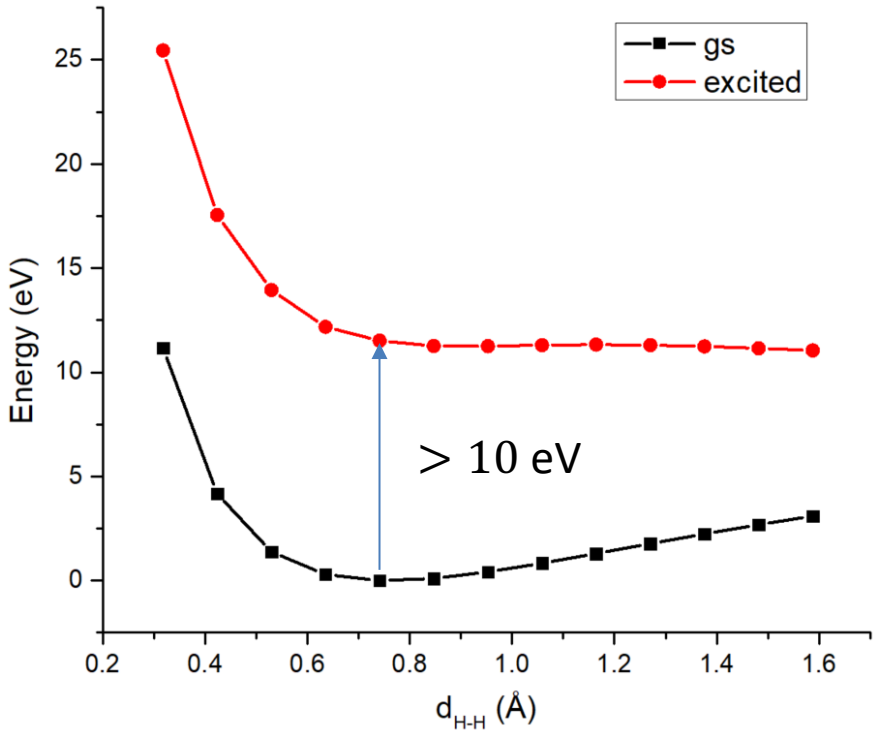


H_2 dissociation as an example

Not applicable to directly excite the H_2

- Far from the visible range





Orbital hybridization:

$$|\Psi_\sigma\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle + |\psi_2\rangle)$$

$$|\Psi_{\sigma^*}\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle - |\psi_2\rangle)$$

$$E_a \gg K_b T$$

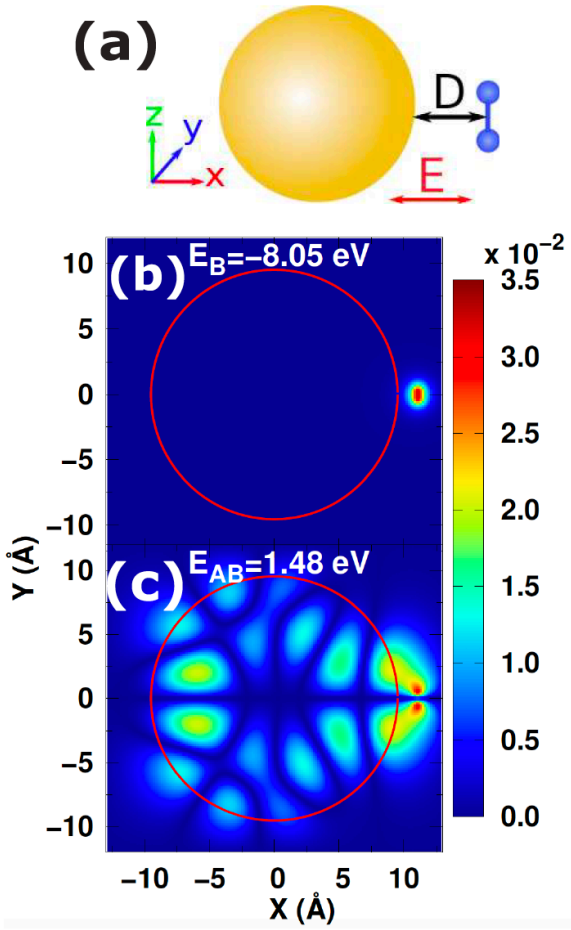
$$k \propto e^{-E_a/K_b T}$$

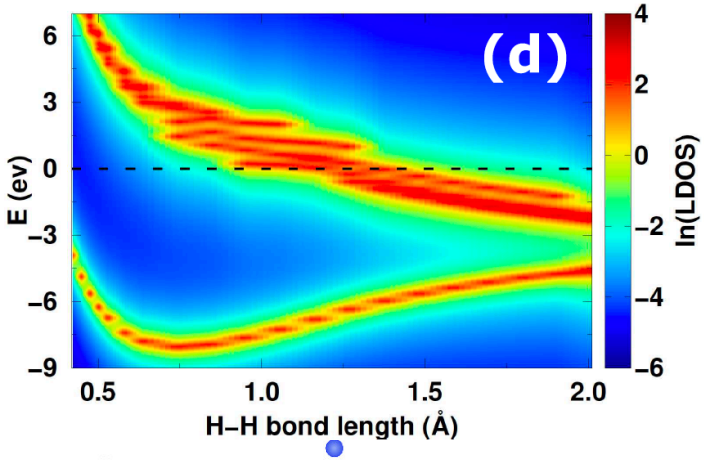
Plasmonic Hot-Carriers Induced H_2 Dissociation (Jellium Model)

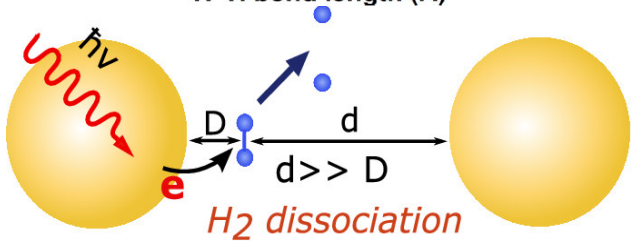
Computational method:

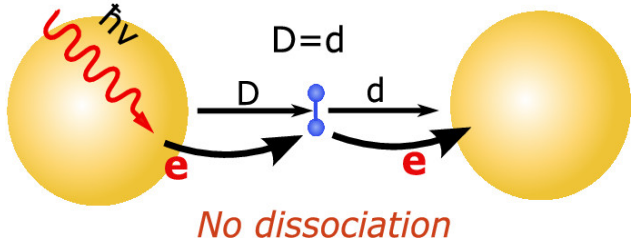
- TDDFT-NAMD (Ehrenfest scheme)
- Jellium model for metallic NP (core electrons and the nuclei are modeled as the uniform positive background)

Diameter of NP is 2 nm, H_2-NP distance 1.59 A.



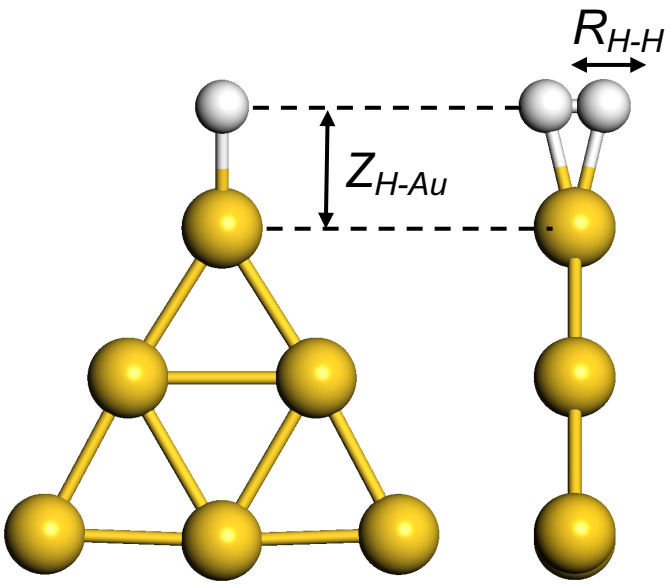




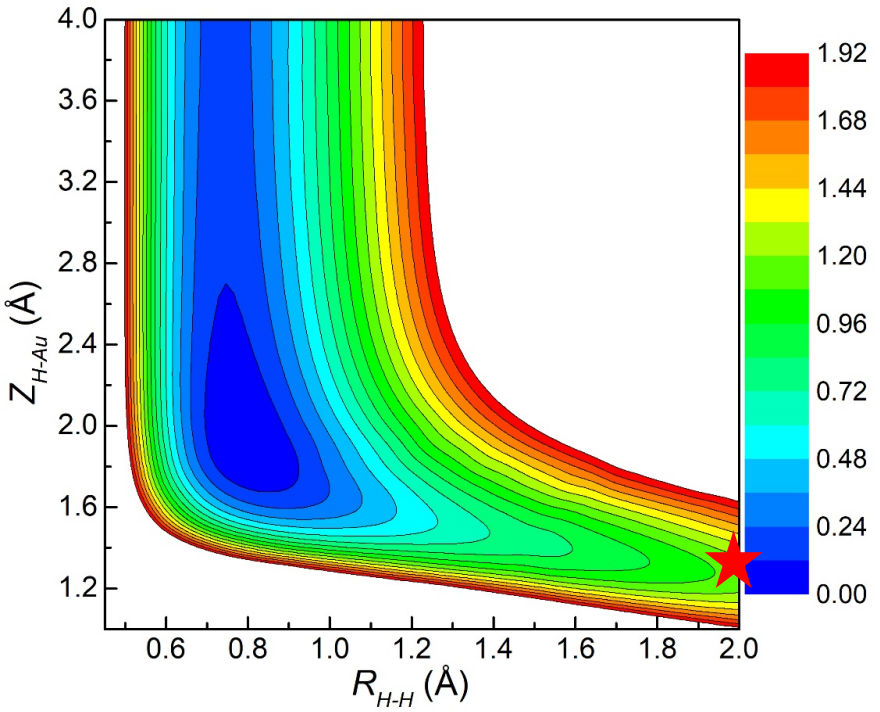


Y. Zhang, T. Nelson, S. Tretiak, GC Schatz, ACS Nano, 12, 8415 (2018)

Atomistic studies of plasmon mediated reactions



- Equilibrium geometry
  - $Z_{H\text{-}Au}$ = 1.91 Å
  - $R_{H\text{-}H}$ = 0.79 Å
  - Adsorption energy: 0.1 eV



H_2 dissociation has a high ground state reaction barrier (marked with red star) of 1.14 eV

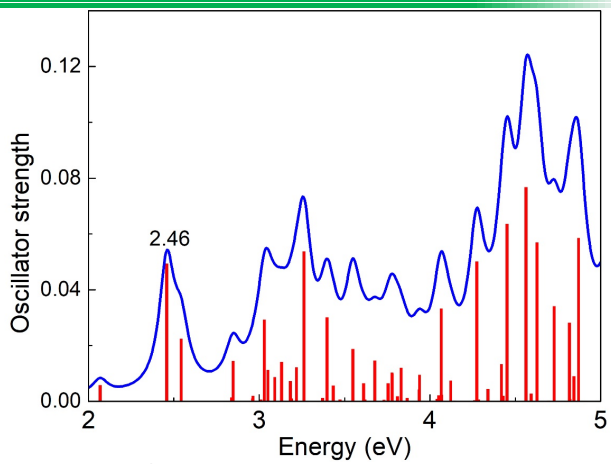
Q. Wu, L. Zhou, G. C. Schatz, Y. Zhang*, H. Guo*, *J. Am. Chem. Soc.* 142, 13090 (2020)

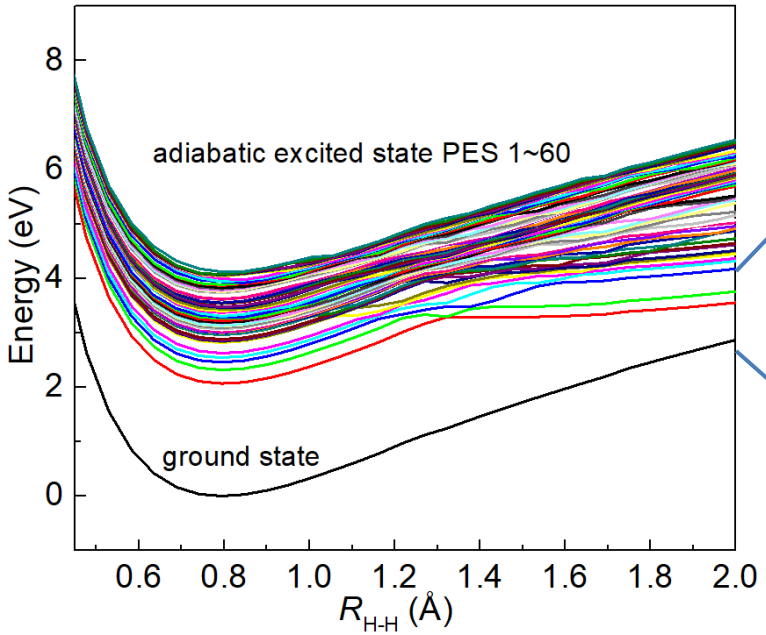
Excited state PES

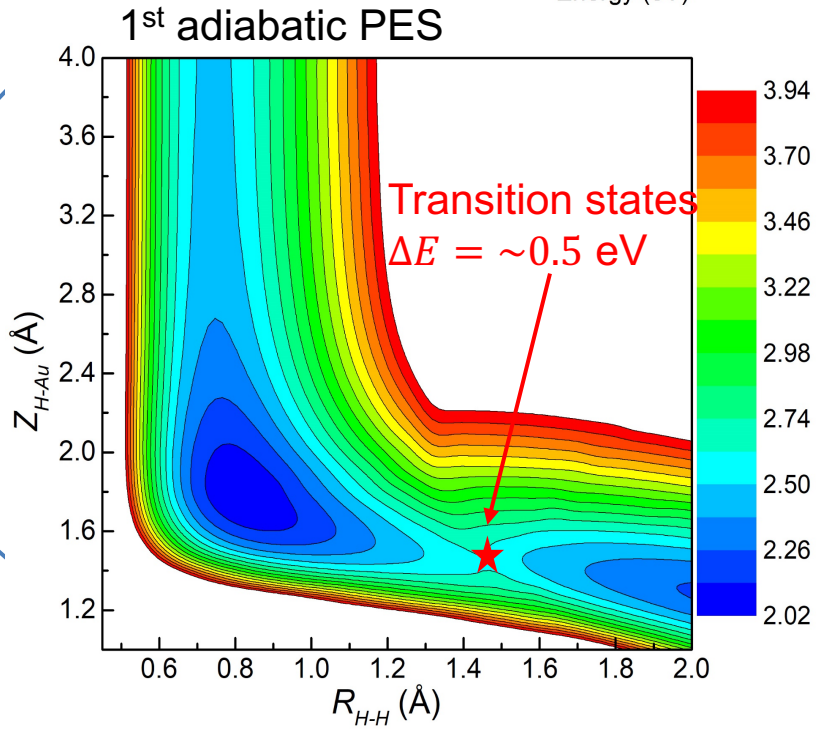
Casida equation

$$\Omega F_I = \omega_I^2 F_I$$

- 68 valence electrons (34 occupied KS orbitals)
- 20 unoccupied KS orbitals are considered
- A total of 680 orbital transitions





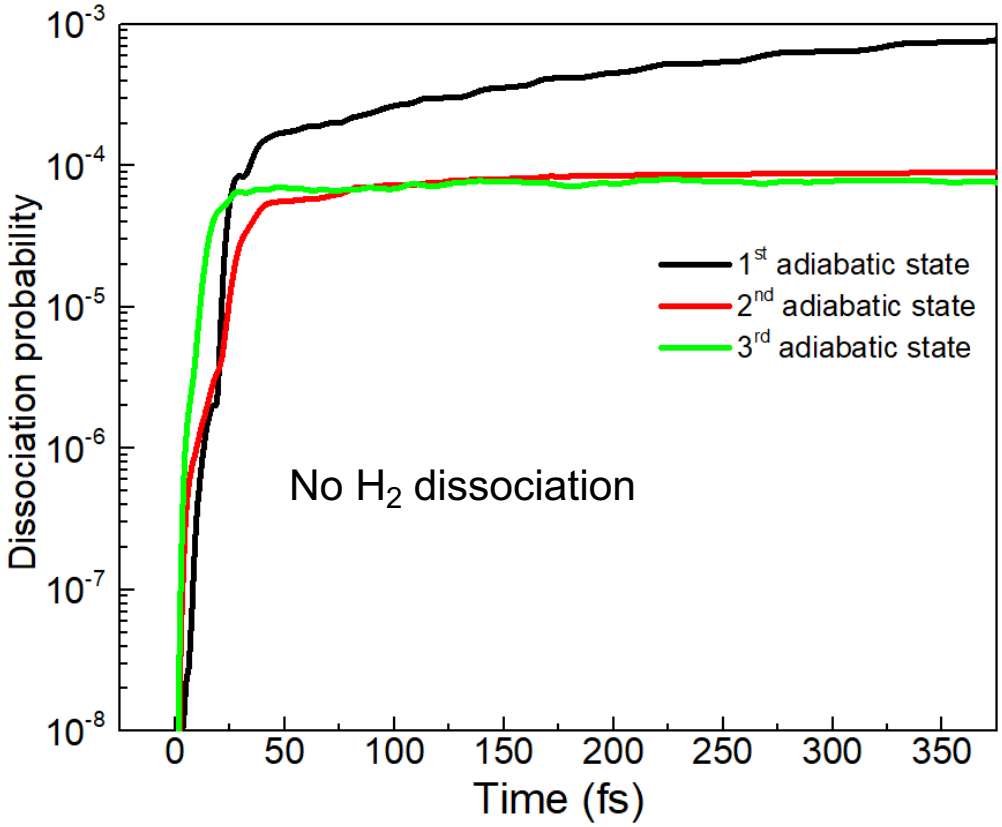


Quantum dynamics on adiabatic PES

Quantum dynamics simulations

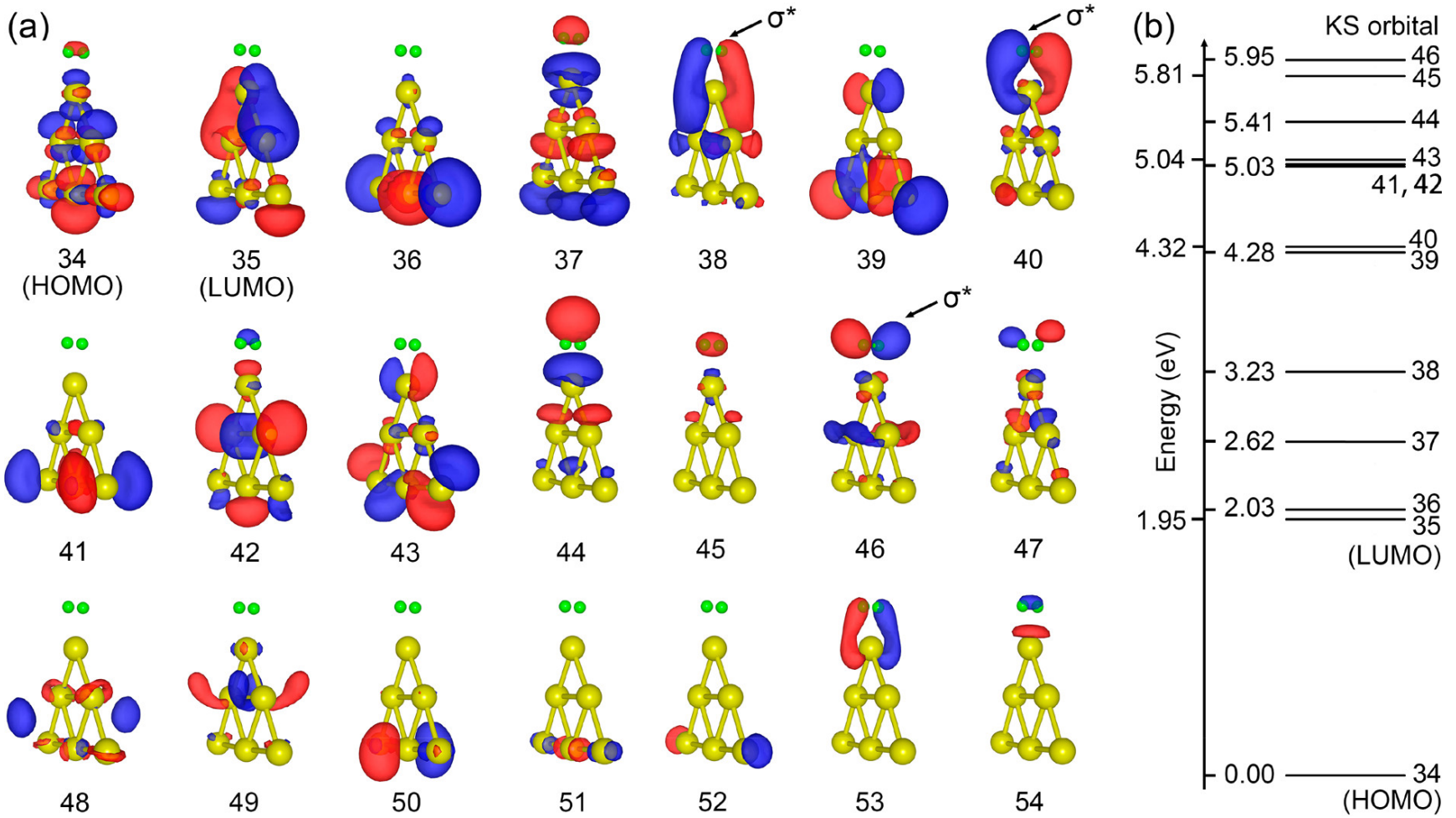
$$H_l = -\frac{1}{2M_R}\frac{\partial^2}{\partial R^2} - \frac{1}{2M_z}\frac{\partial^2}{\partial Z^2} + V_l(R,Z)$$

- R is the bond distance of H_2 molecule
- Z is the distance between the H_2 center-of-mass and surface.
- $V_l(R,Z)$ $(l = g, e)$ are the potential energy



On these adiabatic states, probability for dissociation is very low

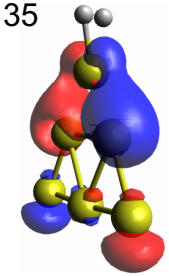
Spatial distribution of HOMO and 20 unoccupied MOs



Only a few MOs have H_2 σ* characteristics!

Excitation energies and corresponding oscillator strengths

35



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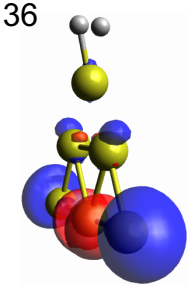
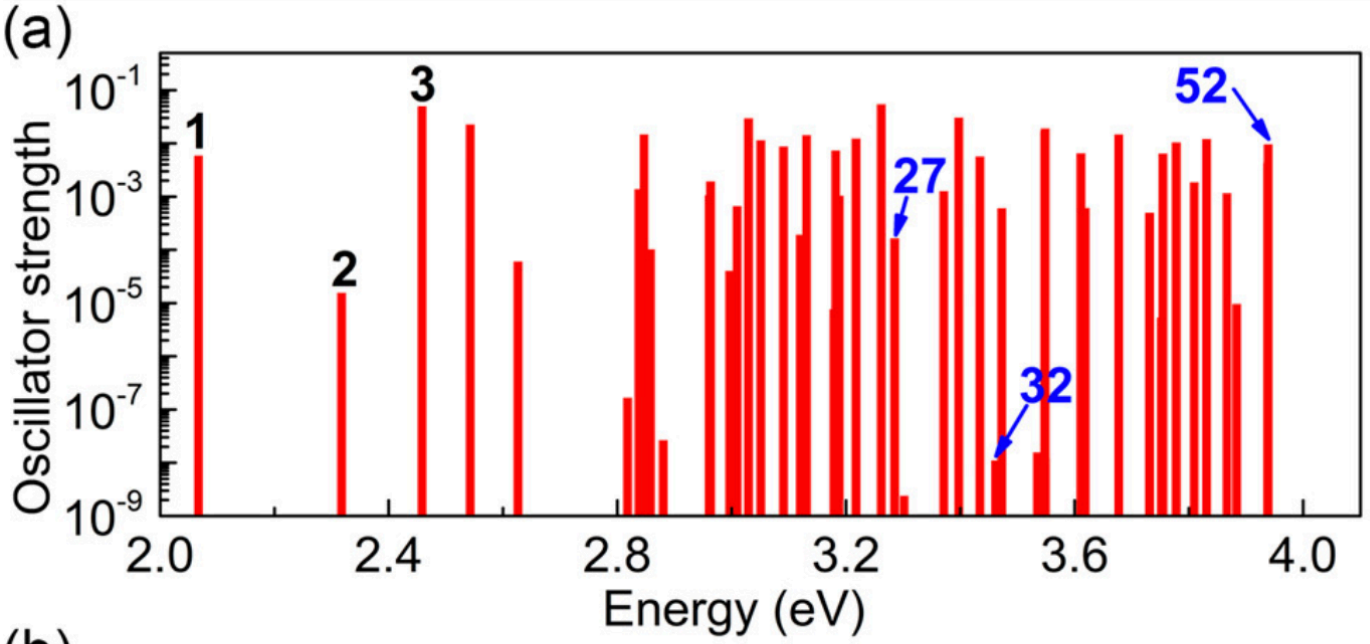


(a)



(b)

Excitation 1

From	To	T_{kl}^2
34	35	0.927
33	36	0.062
Total		0.989

Excitation 2

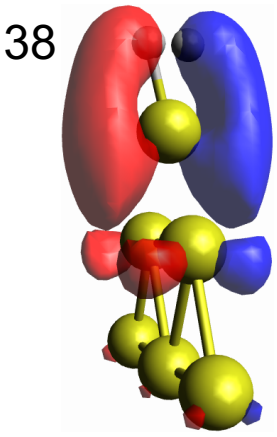
From	To	T_{kl}^2
34	35	0.318
33	36	0.638
Total		0.956

Excitation 3

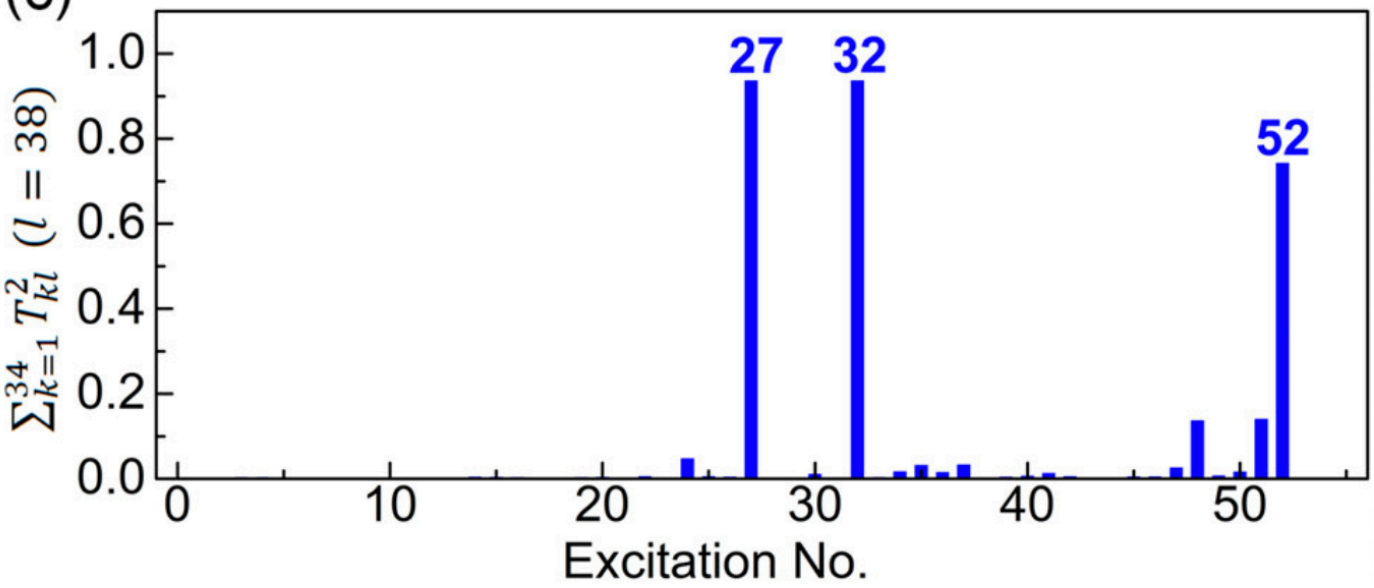
From	To	T_{kl}^2
34	35	0.053
33	36	0.860
Total		0.913

These excitations are likened to HE states in metal nanoclusters.

Excitations with antibonding characteristics of the H_2



(c)



(d)

Excitation 27

From	To	T_{kl}^2
23	35	0.049
34	38	0.930
Total		0.979

Excitation 32

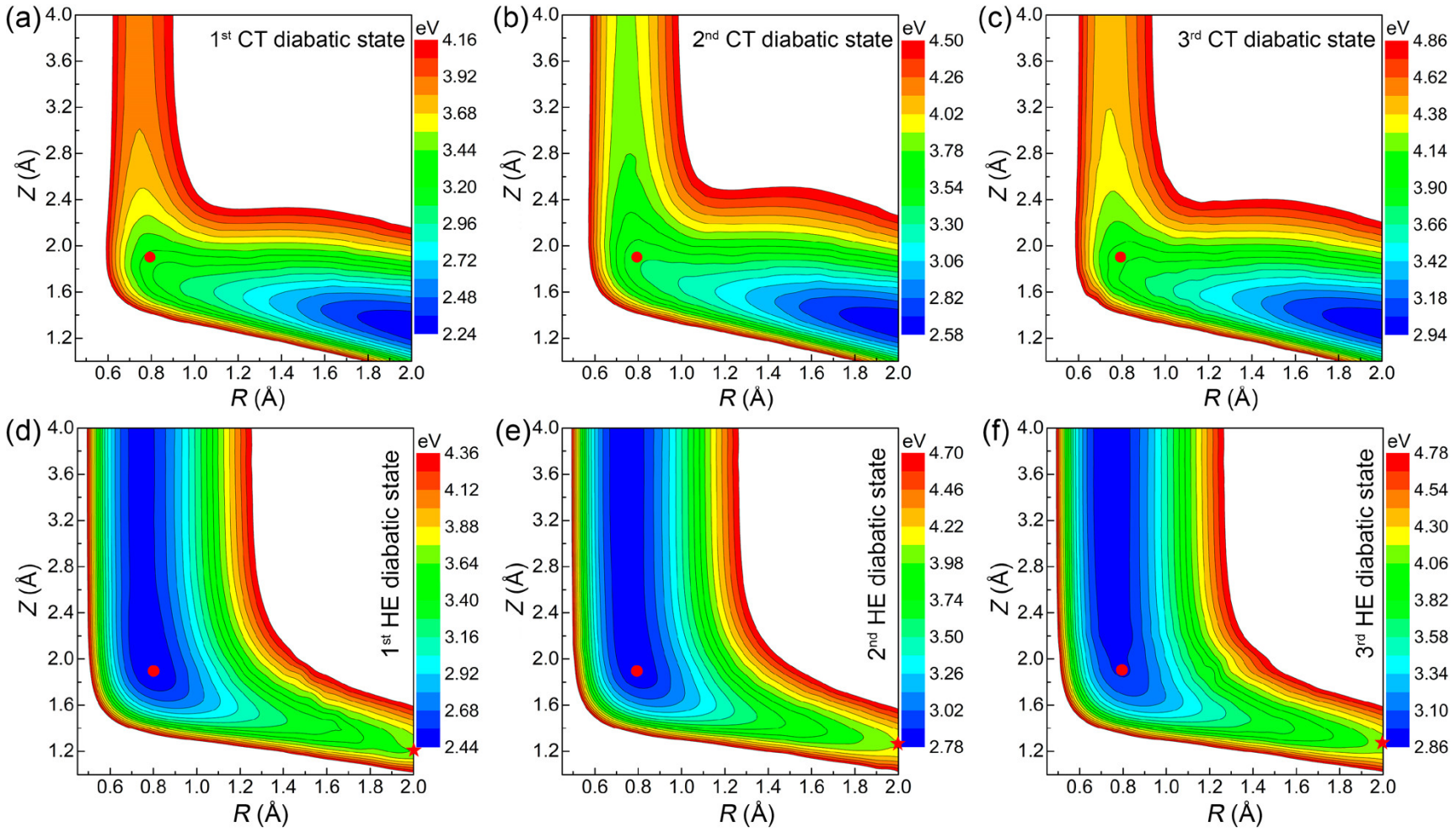
From	To	T_{kl}^2
30	37	0.047
33	38	0.931
Total		0.978

Excitation 52

From	To	T_{kl}^2
15	35	0.124
32	38	0.686
Total		0.810

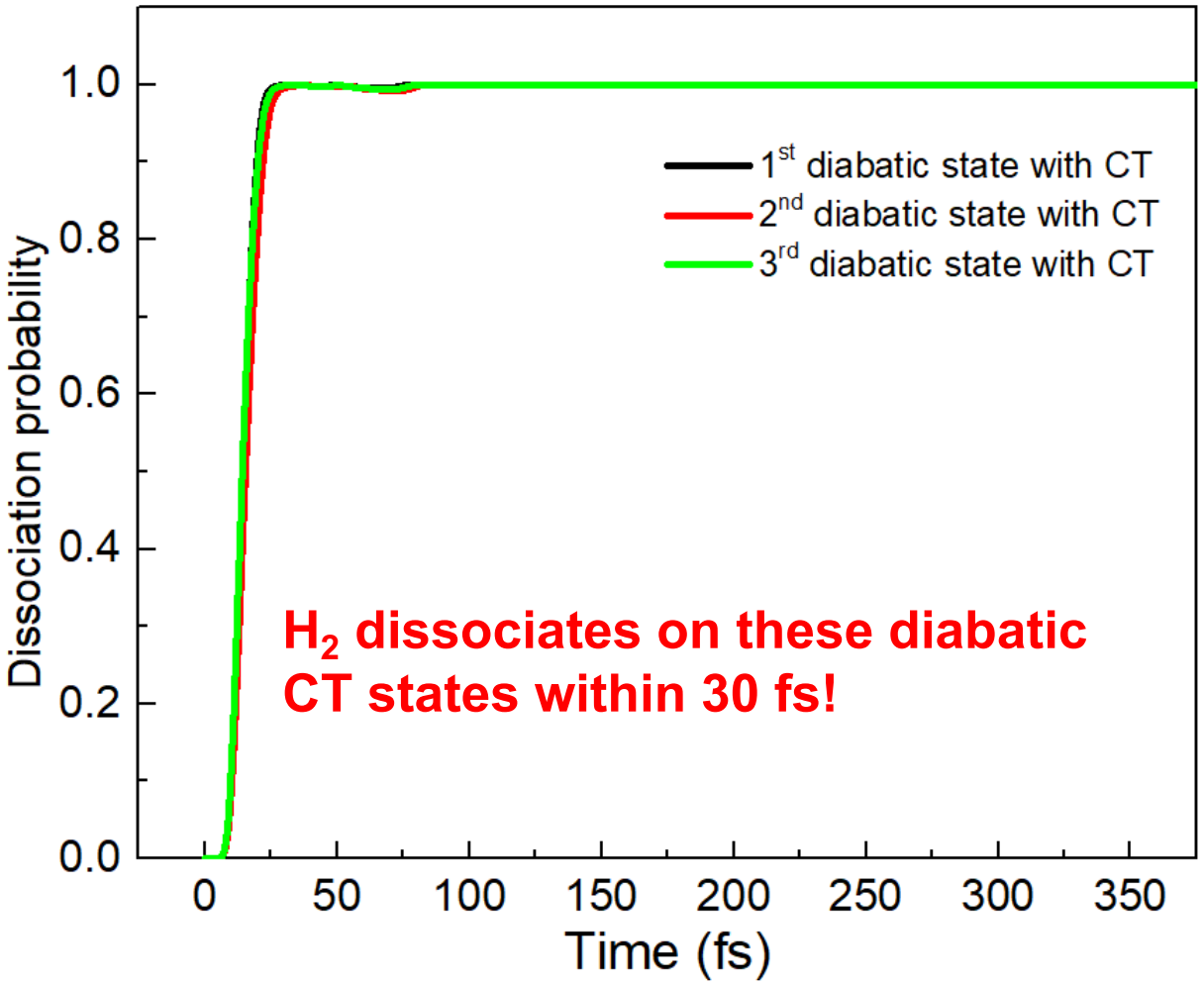
Charge transfer (CT) states

Diabatic HE and CT states



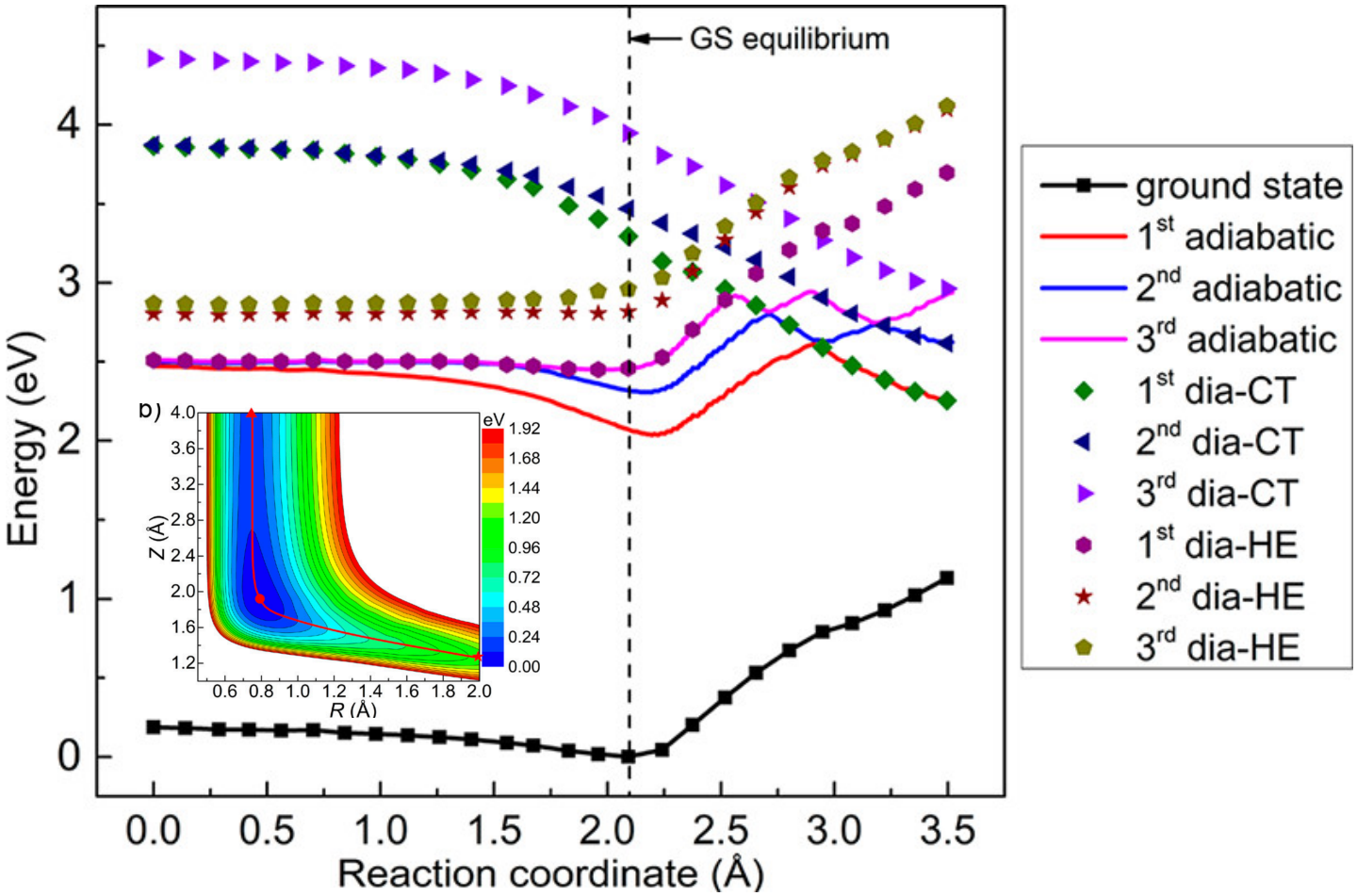
Diabatic CT states have no barrier, while HE states have larger barrier for H_2 dissociation.

Quantum dynamics on the diabatic states with CT



But, CT transitions cannot be accessed directly by the photon for the three lowest absorption peaks

Potential profiles along the minimum energy pathway



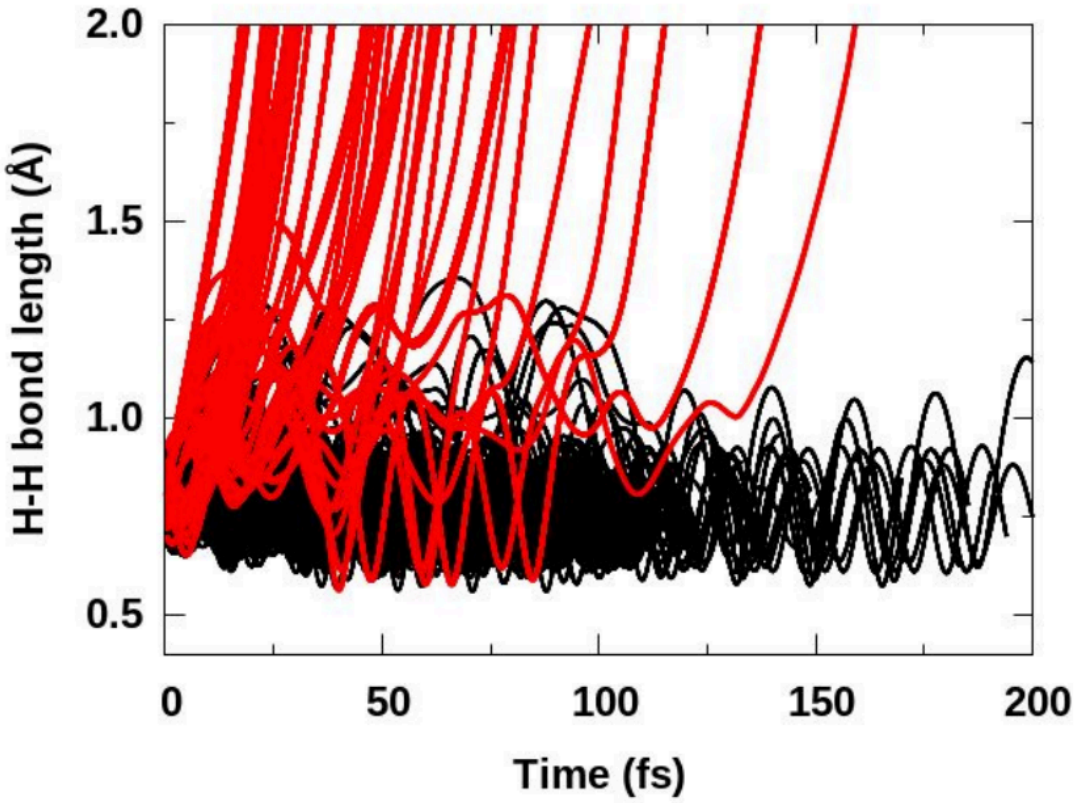
The two different manifolds of nested excited states cross, leading to non-adiabatic transitions

Non-adiabatic Molecular Dynamics (LZ model)

Landau–Zener model in the adiabatic representation:

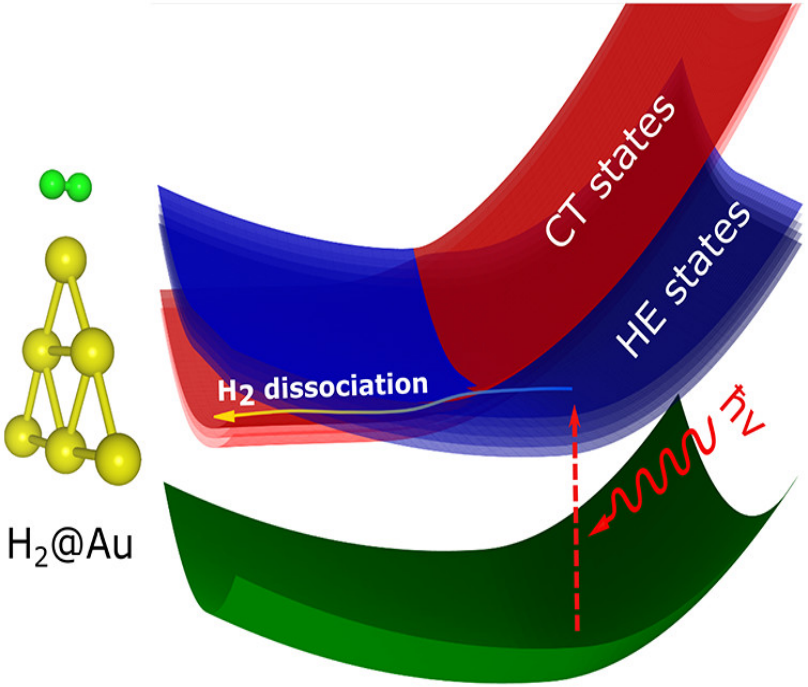
$$P_{ij} = \exp\left(-\frac{\pi\sqrt{m}}{2}\sqrt{\left|\frac{\Delta E_{ij}^3}{\frac{d^2}{dt^2}\Delta E_{ij}}\right|}\right).$$

- A random number $\xi \in [0, 1]$ is generated and hopping is triggered when $\xi > P_{ij}$.
- Velocities are rescaled according to ΔE_{ij} after the hopping.



Among 500 trajectories, 27 led to dissociation of H2 dissociation, giving a probability of 5.4%

Summary & Future works

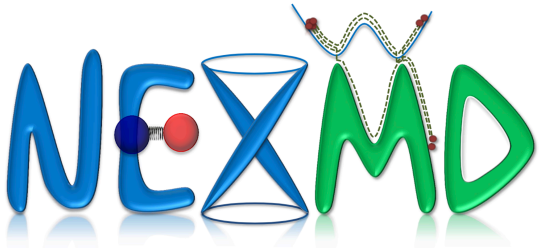


Physical picture of the plasmon mediated H_2 dissociation:

- A dense manifold of adiabatic excited states (dominated by HE states) are excited by plasmon
- Non-adiabatic transition from HE to CT states facilitates chemical reactions

Future direction:

- DFTB-NEXMD for simulating chemical reactions on realistic plasmonic NPs (>200 atoms): a) plasmon excitation; b) charge-transfer c) hot electron relaxation, d) heating..



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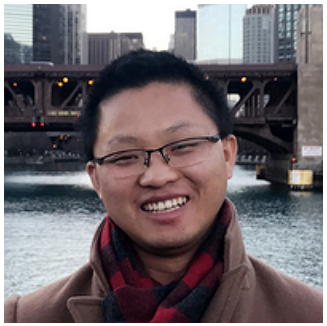

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