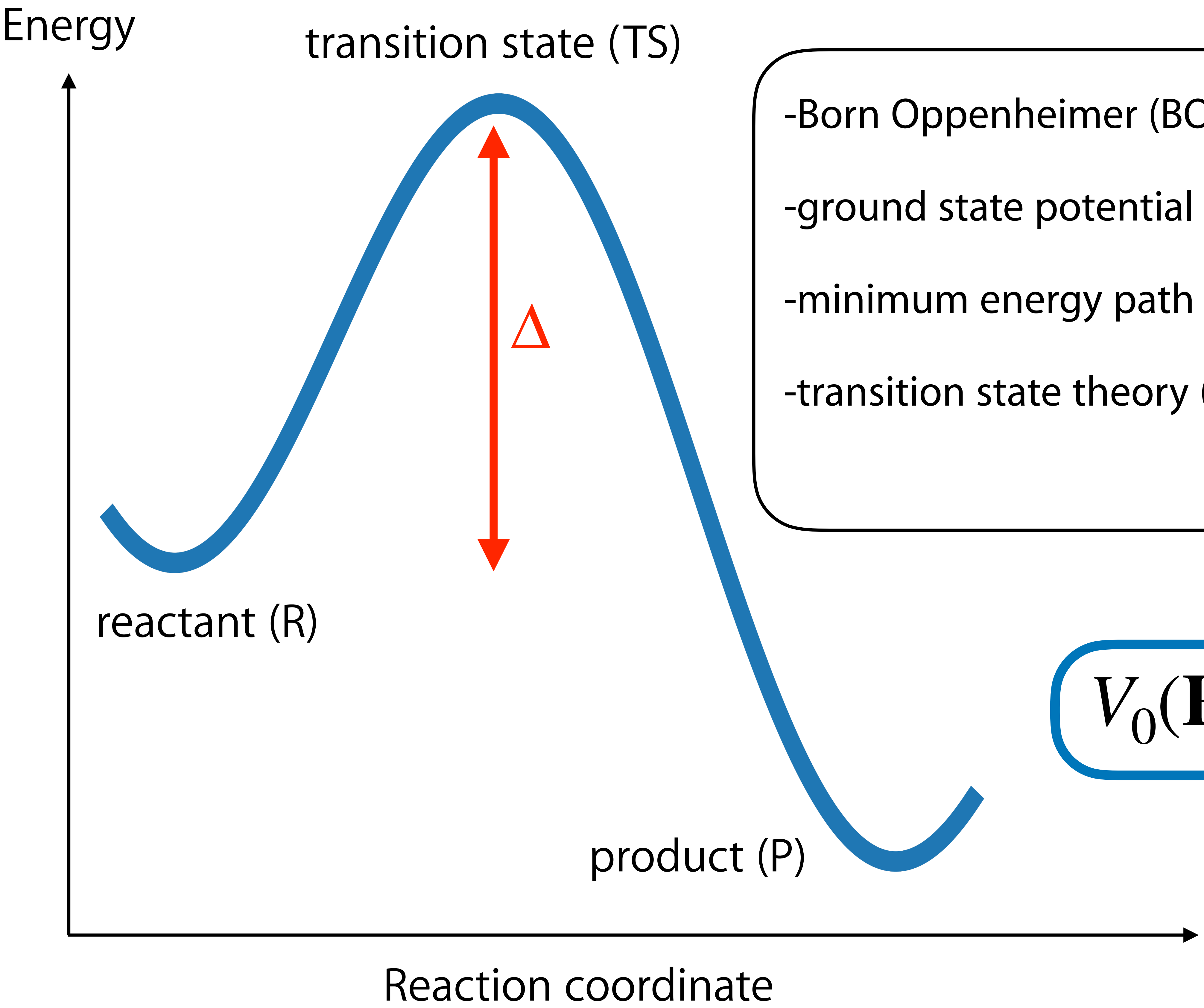
Universidad Autónoma
de Madrid

Cavity-modified ground-state chemical reactivity

Clàudia Climent

Departamento de Física Teórica de la Materia Condensada
Universidad Autónoma de Madrid

Chemical reaction



-Born Oppenheimer (BO) approximation

-ground state potential energy surface (PES)

-minimum energy path

-transition state theory (TST)

$$k \propto e^{-\Delta/RT}$$

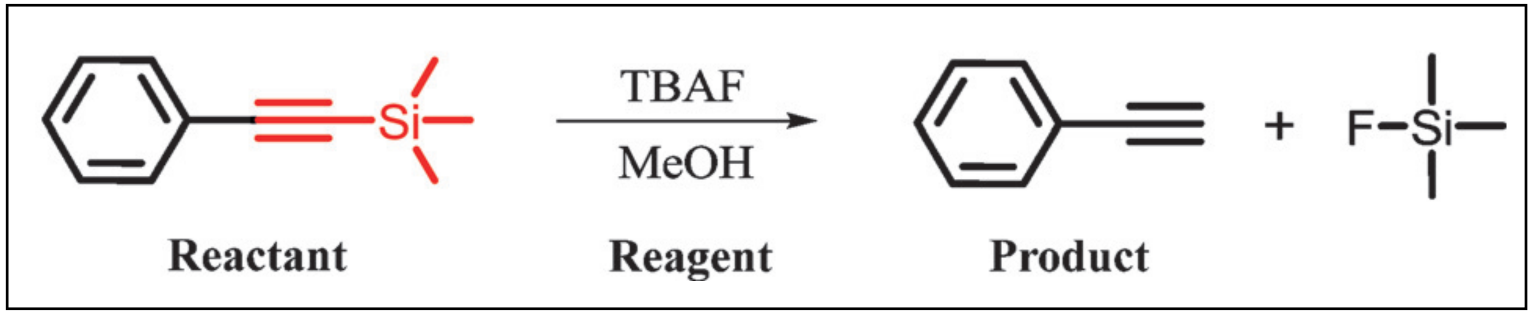
$$\boxed{V_0(\mathbf{R})}$$

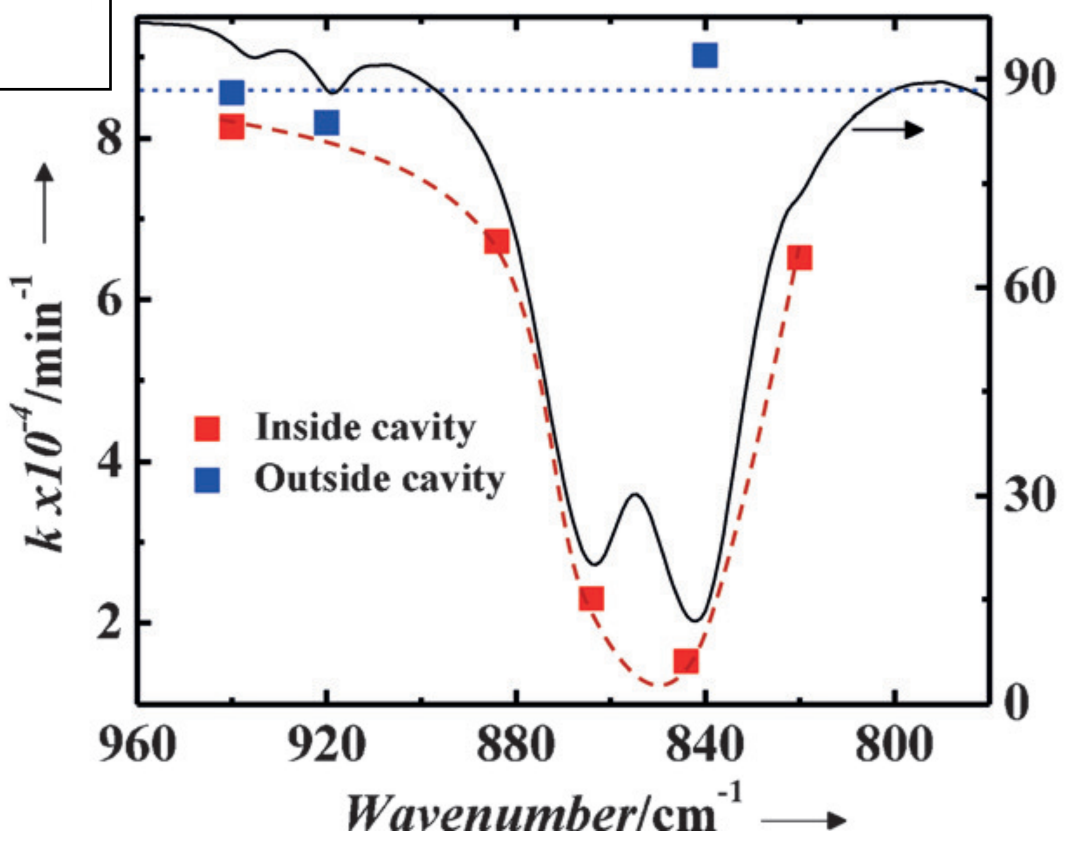
Motivation: Experimental evidence of modified chemical reactivity with vibrational strong coupling

Thomas Ebbesen group & coworkers

Ground-State Chemical Reactivity under Vibrational Coupling to the Vacuum Electromagnetic Field

Angew .Chem .Int. Ed. **2016**, 55, 11462





Motivation: Experimental evidence of modified chemical reactivity with vibrational strong coupling

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Ground-State Chemical Reactivity under Vibrational Coupling to the Vacuum Electromagnetic Field
Angew .Chem .Int. Ed. **2016**, 55, 11462

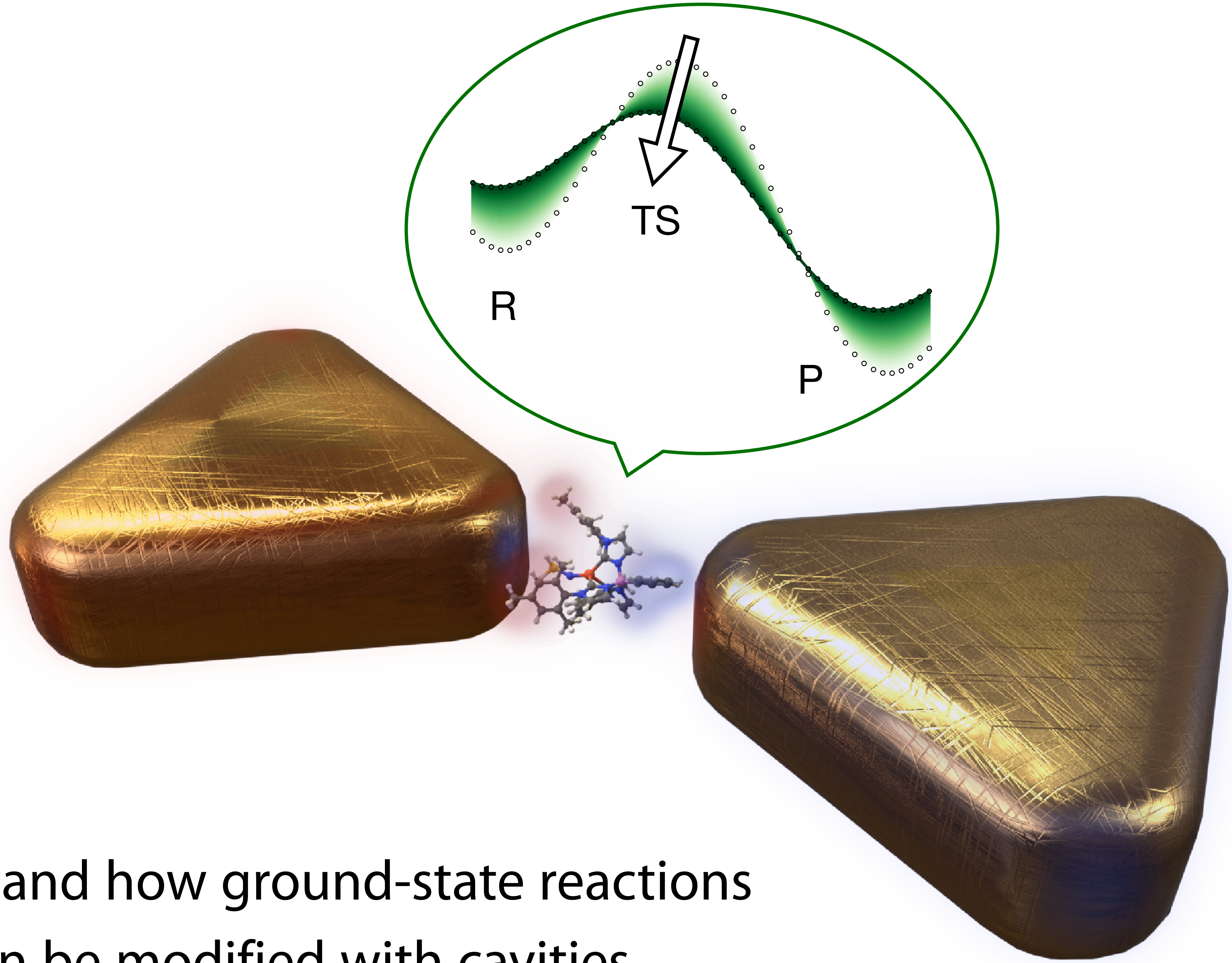
Tilting a ground-state reactivity landscape by vibrational strong coupling
Science **2019**, 363, 615

Cavity Catalysis by Cooperative Vibrational Strong Coupling of Reactant and Solvent Molecules
Angew .Chem .Int. Ed. **2019**

Cavity Catalysis -Accelerating Reactions under Vibrational Strong Coupling
2018 doi:10.26434/chemrxiv.7234721.v3.

Modification of enzyme activity by vibrational strong coupling of water
2019 https://nano.isis.unistra.fr/publications/

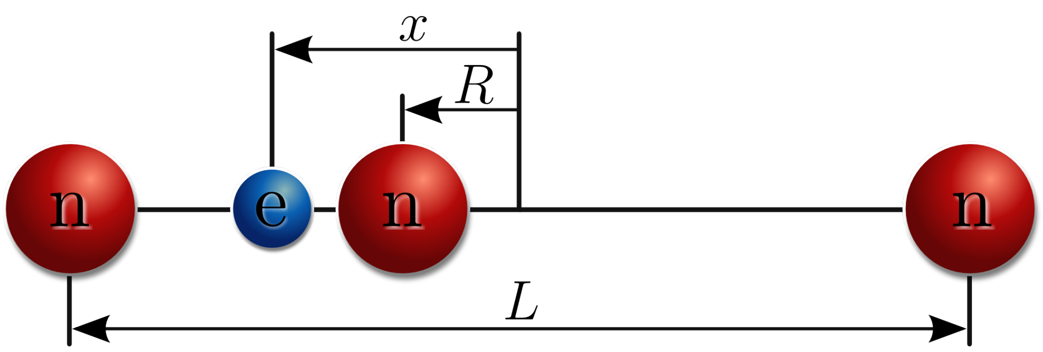
Goal



understand how ground-state reactions can be modified with cavities

Theoretical model: simplified molecule

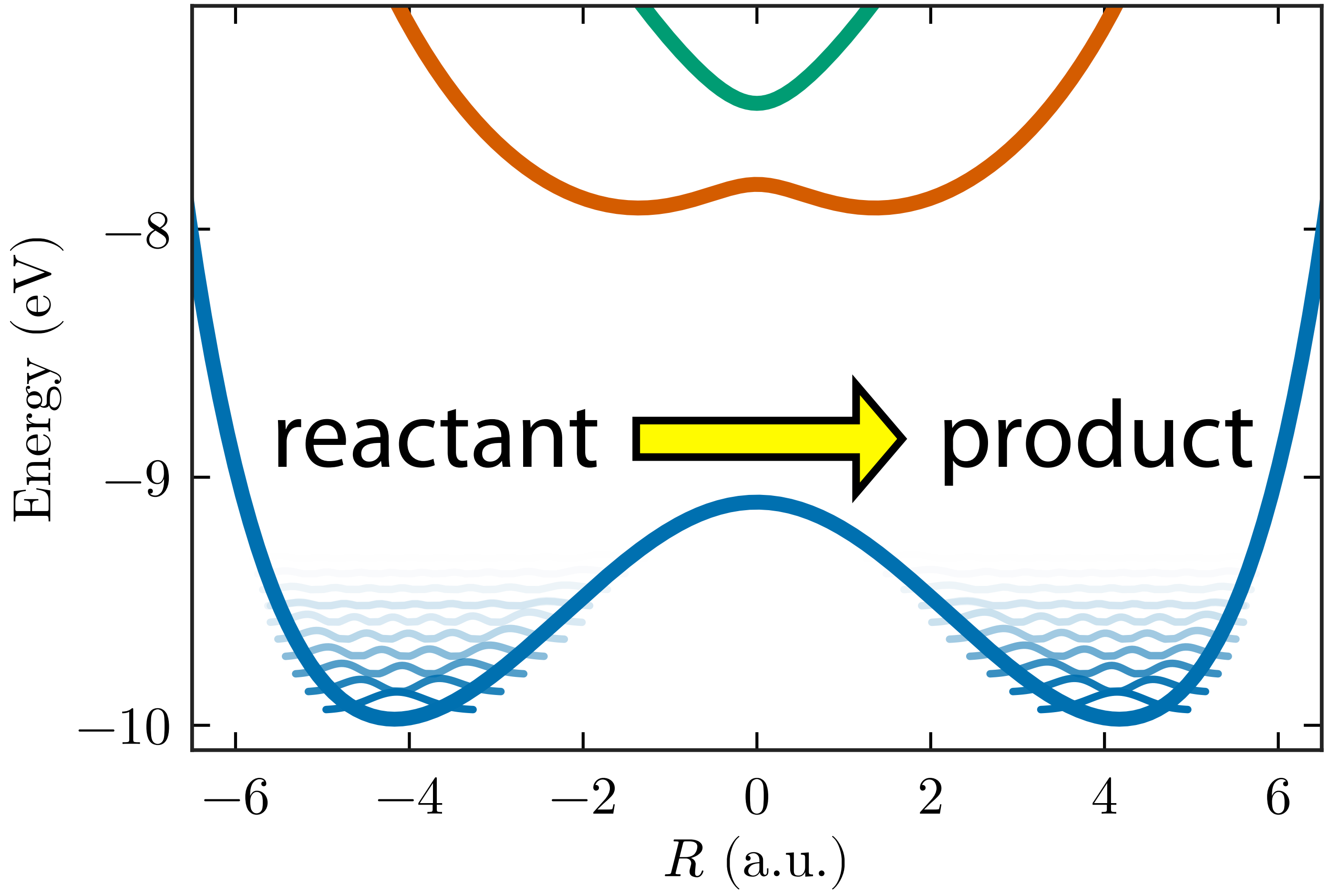
Javier Galego



Shin-Metiu model

$$\hat{H} = \hat{T}_n + \hat{H}_e(\hat{\mathbf{x}}, \hat{\mathbf{R}})$$

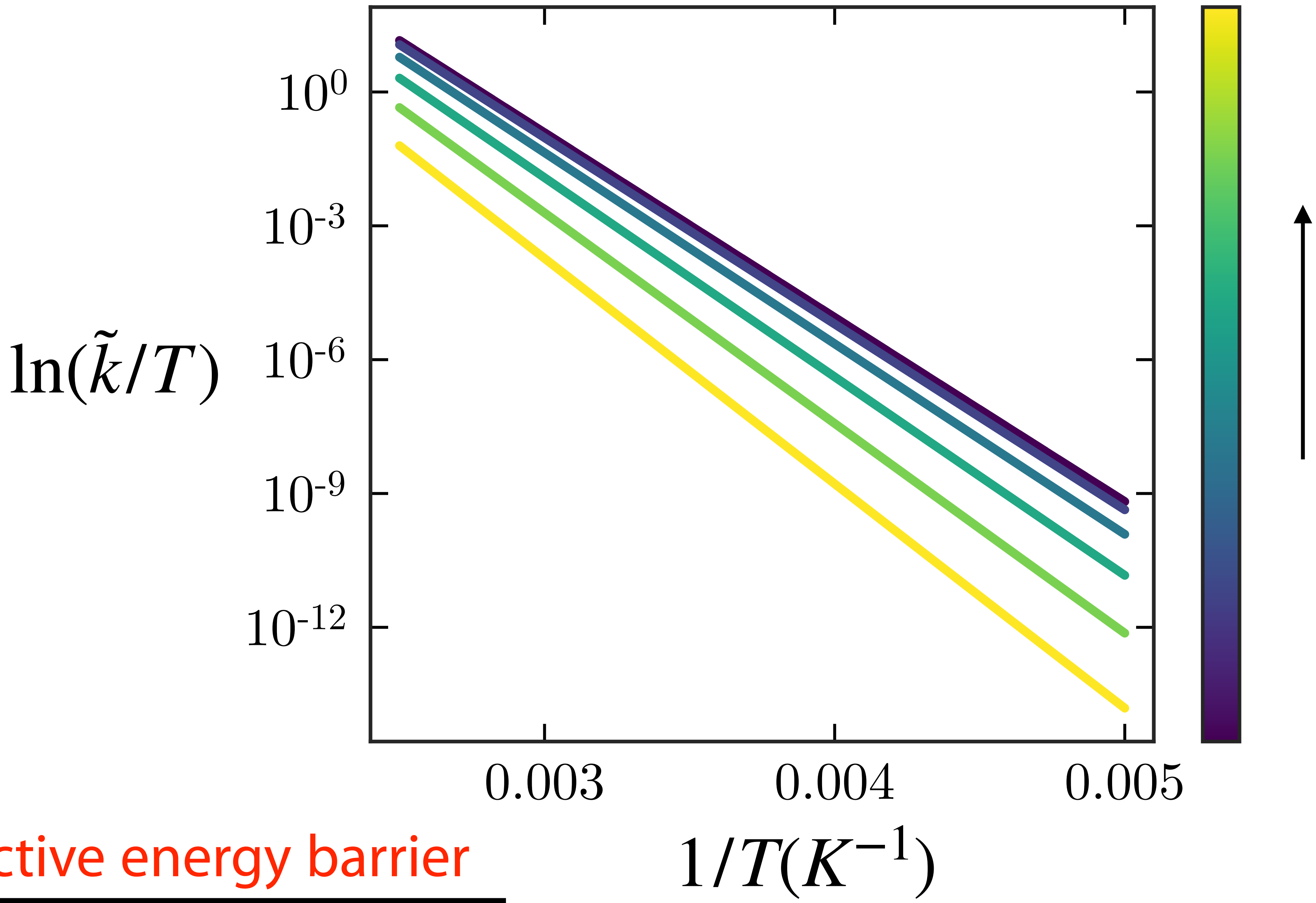
Shin & Metiu, J. Chem. Phys., 102, 23 (1995)



coupled light-matter system: compute **quantum reaction rate**

$$\hat{H} = \hat{T}_n + \hat{H}_e(\hat{\mathbf{x}}, \hat{\mathbf{R}}) + \omega_c \hat{a}^\dagger \hat{a} + \hat{\boldsymbol{\mu}}(\hat{\mathbf{x}}, \hat{\mathbf{R}}) \cdot \boldsymbol{E}_{1ph}(\hat{a}^\dagger + \hat{a})$$

Arrhenius plot



coupling strength

effective energy barrier

$$\boxed{\tilde{k} \propto e^{-\frac{E_{barrier}}{k_B T}}}$$

slope changes
∴ energy landscape modified

Recap

Shin-Metiu model:

solved full Hamiltonian & quantum reaction rate

$$\tilde{k} \propto e^{-\frac{E_{barrier}}{k_B T}}$$

effective energy barrier

Real molecules

potential energy surface (PES)

transition state theory (TST)

⇩

Cavity Born-Oppenheimer approximation

Cavity Born-Oppenheimer Approximation (CBOA)

"trick"

cavity EM mode:
explicit harmonic oscillator

e.g. nanoparticle: p, q describe collective motion of electrons

$$\omega_c \hat a^\dagger \hat a = \frac{\hat p^2}{2} + \frac{1}{2}\omega_c^2 \hat q^2$$

$$\hat a^\dagger + \hat a = \sqrt{2\omega_c}\,\hat q$$

standard BOA: "separate" electronic & nuclear motions

cavity BOA: cavity mode treated as a 'slow' nuclear DOF

$$\hat H_e(\hat{\mathbf x};\hat{\mathbf R},q) = \hat H - \frac{\hat p^2}{2} - \hat T_n = \hat H_e(\hat{\mathbf x};\mathbf R) + \frac{1}{2}\omega_c^2 q^2 + \omega_c q\,\boldsymbol\lambda\cdot\hat{\boldsymbol\mu}(\hat{\mathbf x};\mathbf R)$$

$\tilde V_0(\mathbf R, q)$ electronic CBO PES parametric in R and q

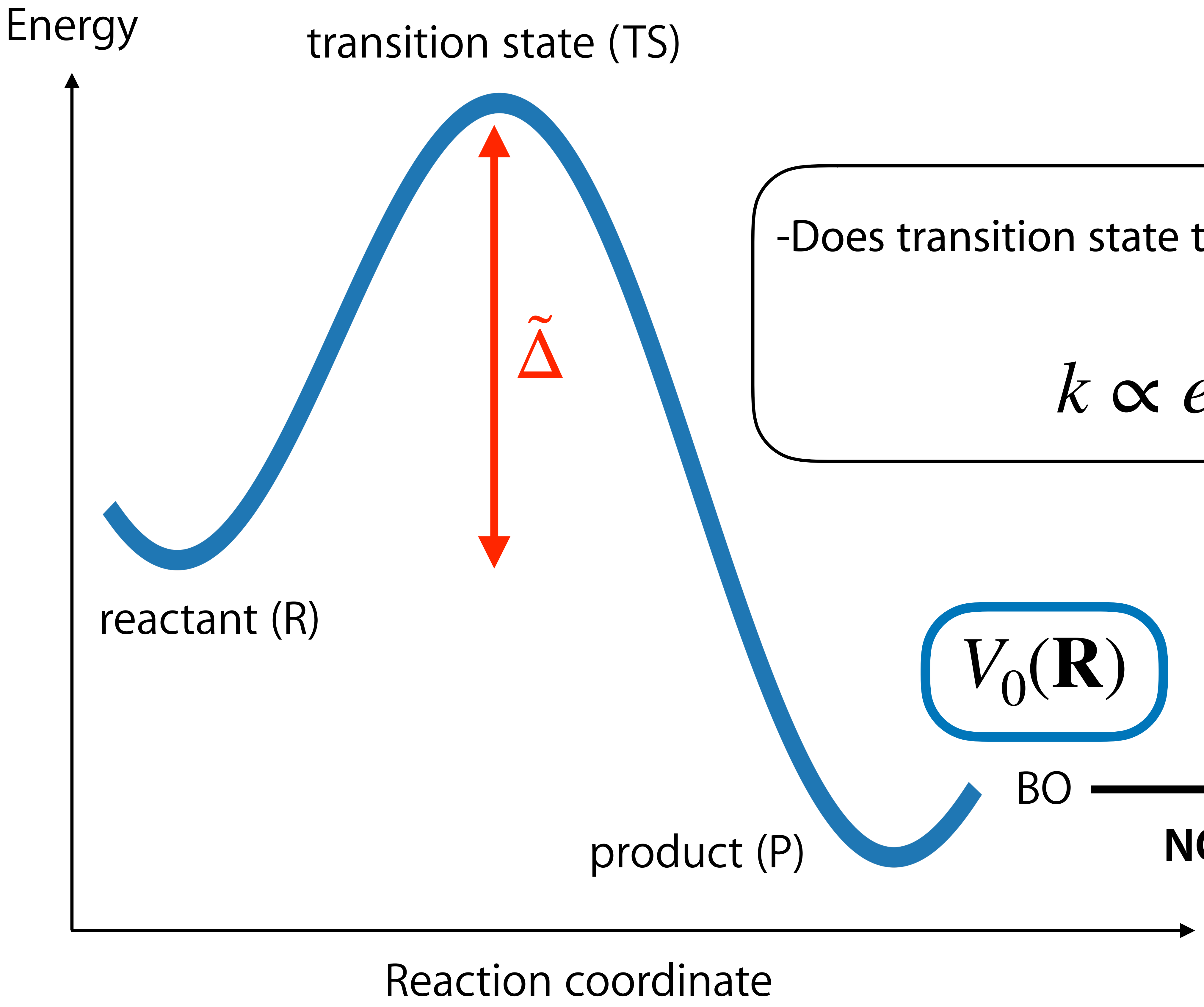
$$\boldsymbol{E}_{1ph} = \sqrt{\frac{\omega_c}{2}}\,\lambda$$

λ coupling strength

normal modes include vibro-polaritons

J. Flick et al., J. Chem. Theory Comput., 13, 1616 (2017)

Chemical reaction



-Does transition state theory (TST) hold?

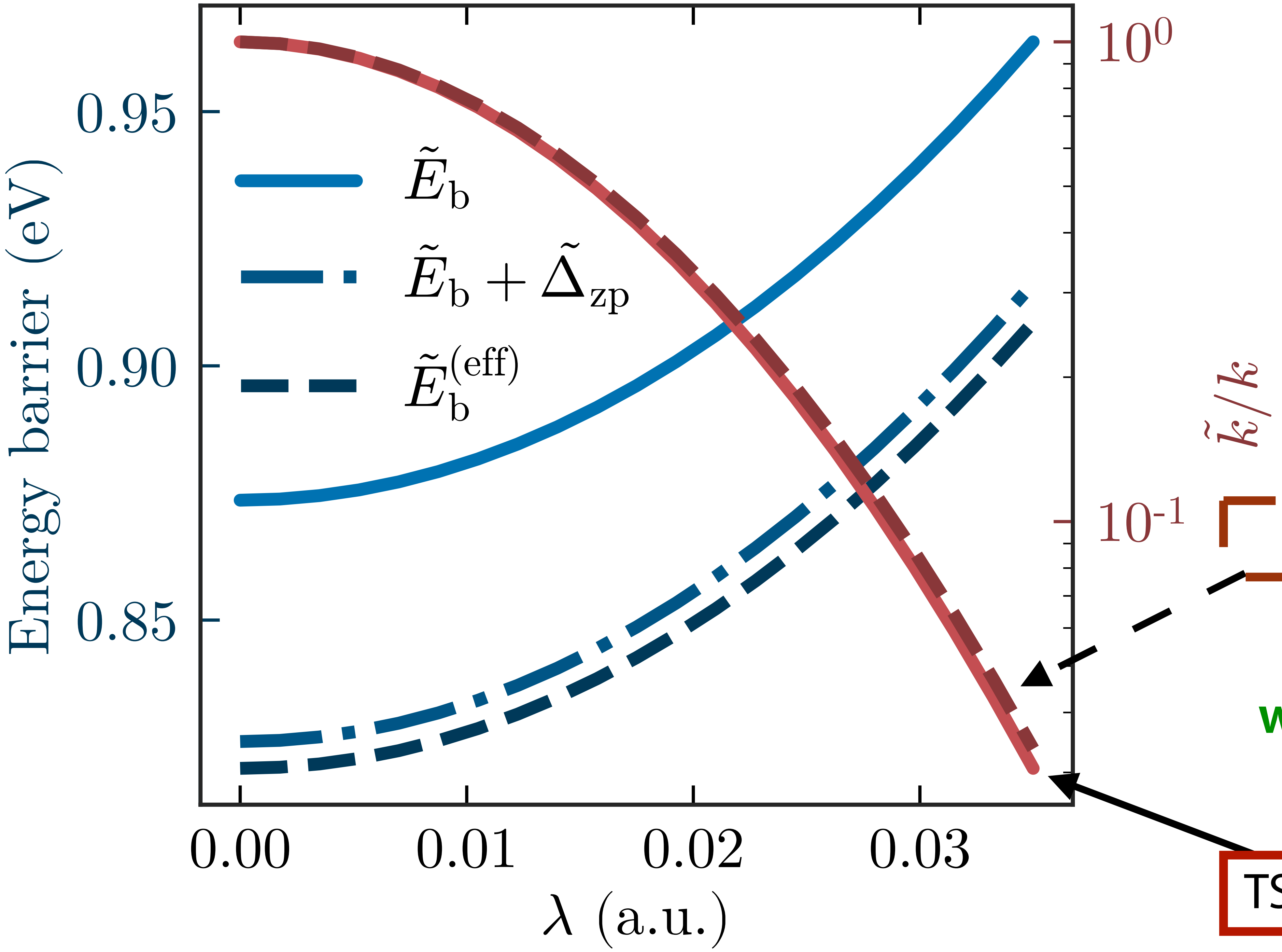
$$k \propto e^{-\tilde{\Delta}/RT}$$

$$\boxed{V_0(\mathbf{R})} \qquad \boxed{\tilde{V}_0(\mathbf{R}, q)}$$

BO → CBO

NOW

Quantum rate vs CBO + TST



quantum rate

we can apply TST

TST with CBO barrier

Perturbation theory: CBO ground state (GS) PES

real molecules (quantum chemistry): simple expression for ground state PES

- -bare molecule GS PES
- -GS permanent dipole moment
- -GS static polarizability

perturbation theory $O(\lambda^2)$

CBO PES PES

$$\tilde{V}_0(\mathbf{R}, q) \approx V_0(\mathbf{R}) + \frac{1}{2}\omega_c^2 q^2 + \lambda \omega_c q \mu_0(\mathbf{R}) - \frac{1}{2}\lambda^2 \omega_c^2 q^2 \alpha_0(\mathbf{R})$$

Minimum energy path: simple analytical expression along q_{min}

$$V_{eff}(\mathbf{R}) = V_0(\mathbf{R}) - \frac{\lambda^2}{2}\mu_o^2(\mathbf{R}) - \frac{\omega_c \lambda^2}{4}\alpha_0(\mathbf{R})$$

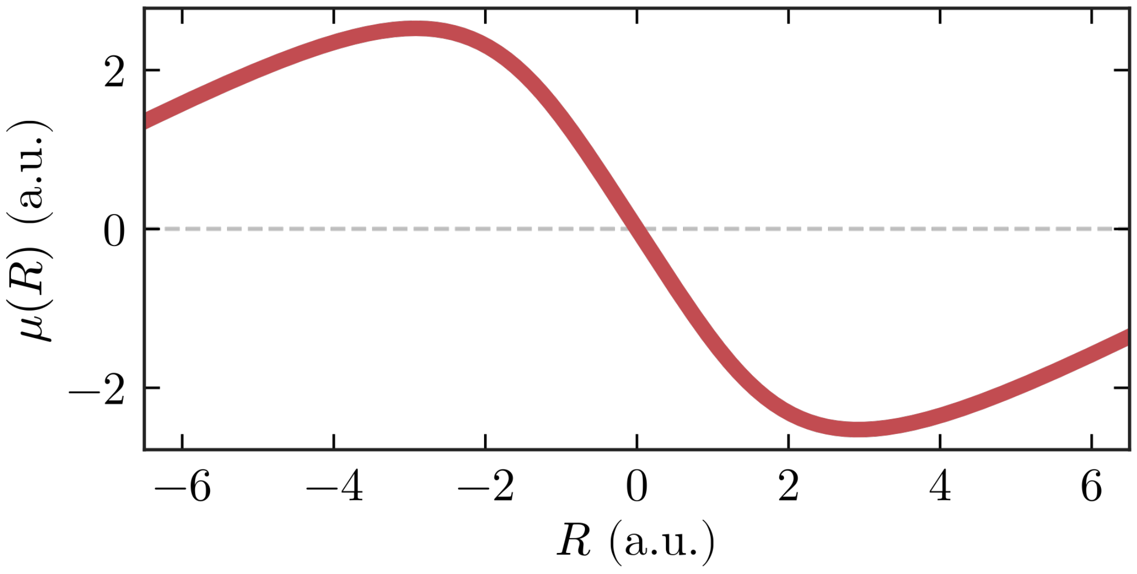
Debye-like potential
(electrostatic)

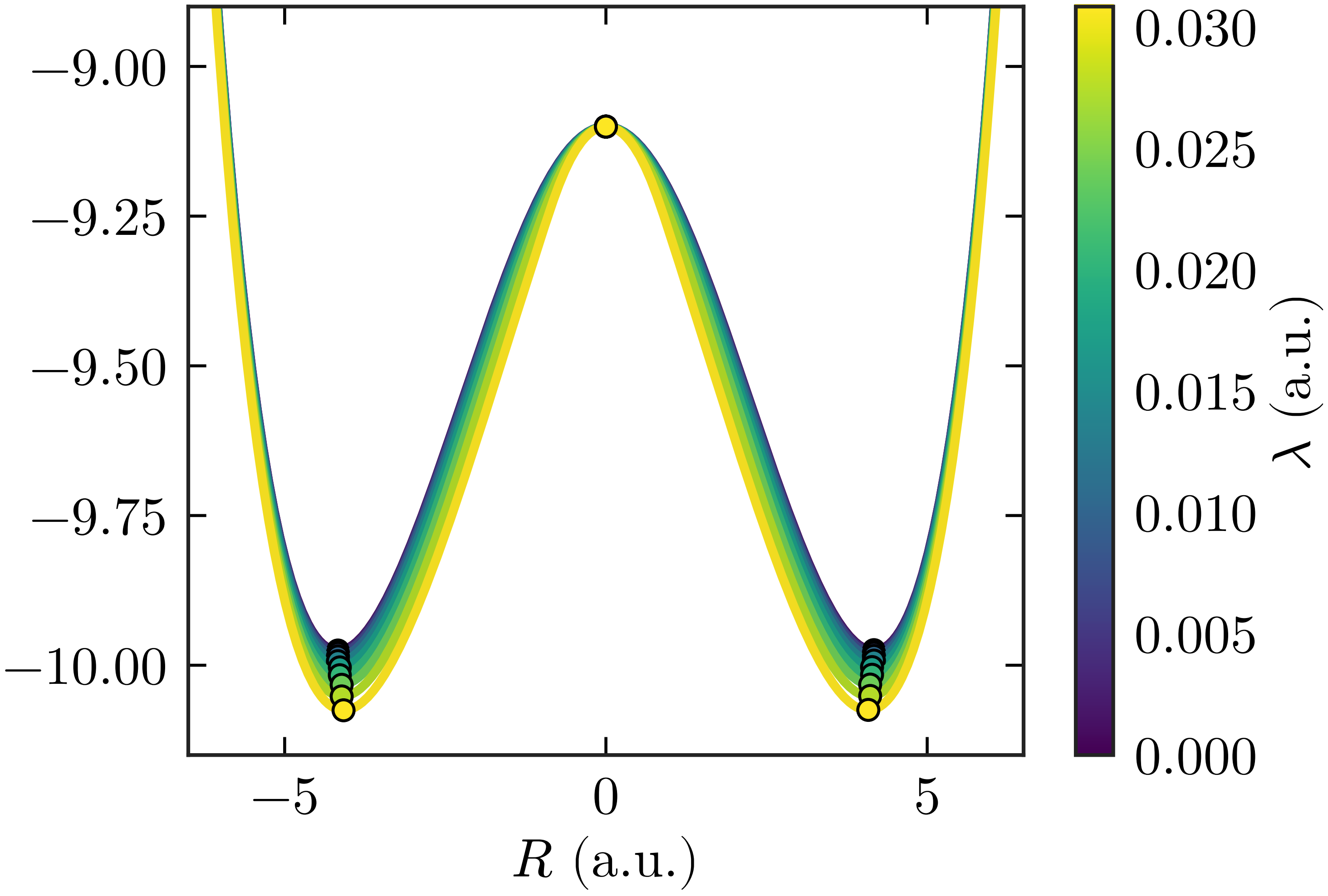
London-like potential
(fluctuations - Casimir-Polder)

Going back to the Shin-Metiu results…

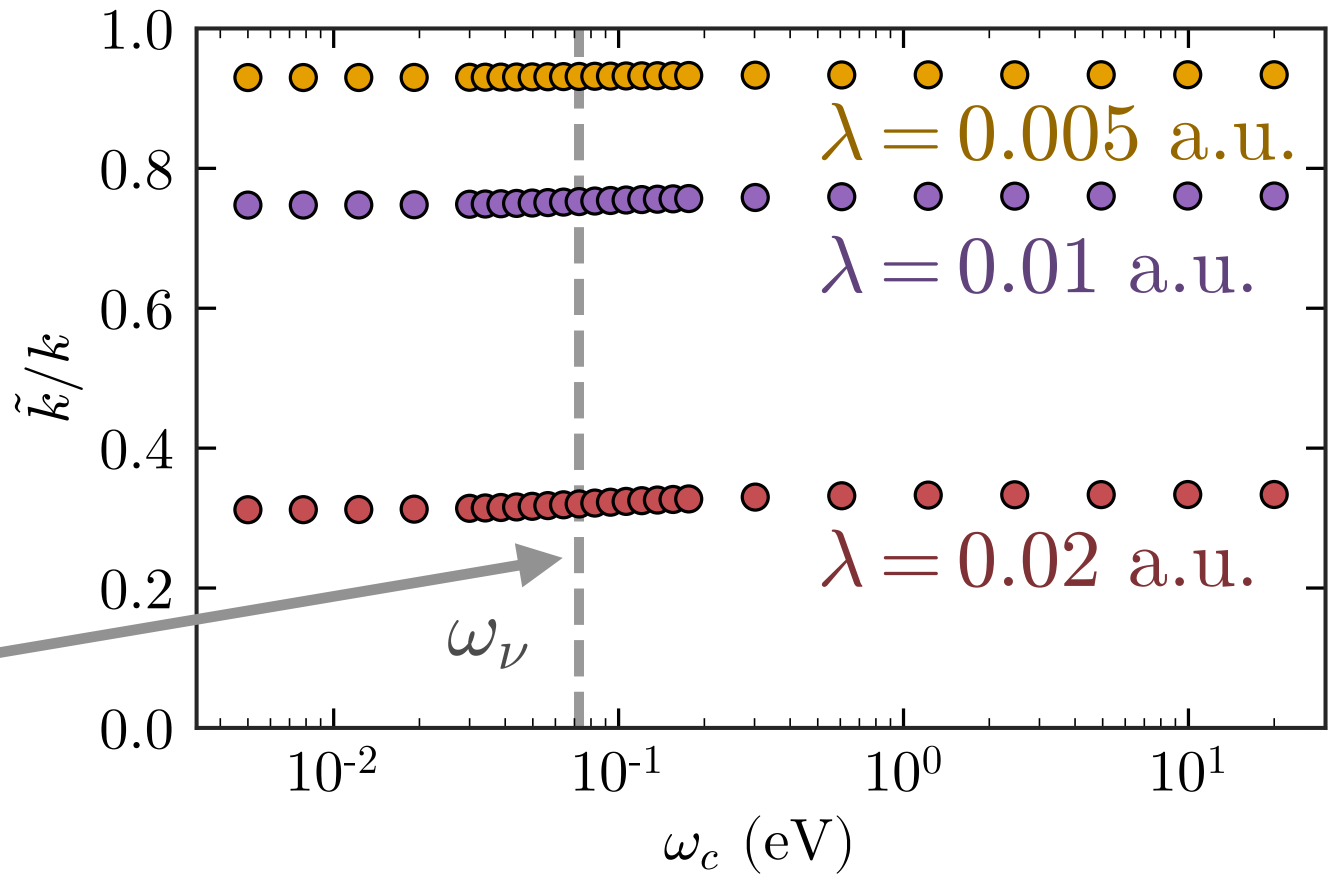
….we can now understand changes in reaction rate

$$V_{eff}(\mathbf{R}) = V_0(\mathbf{R}) - \frac{\lambda^2}{2}\mu_o^2(\mathbf{R}) - \frac{\omega_c\lambda^2}{4}\alpha_0(\mathbf{R})$$





Resonance? (Quantum) Rate vs cavity frequency



Shin-Metiu vibrational frequency

No resonance effect

-strong coupling / formation of vibropolaritons is not relevant

-consistent with “normal” chemistry /TST

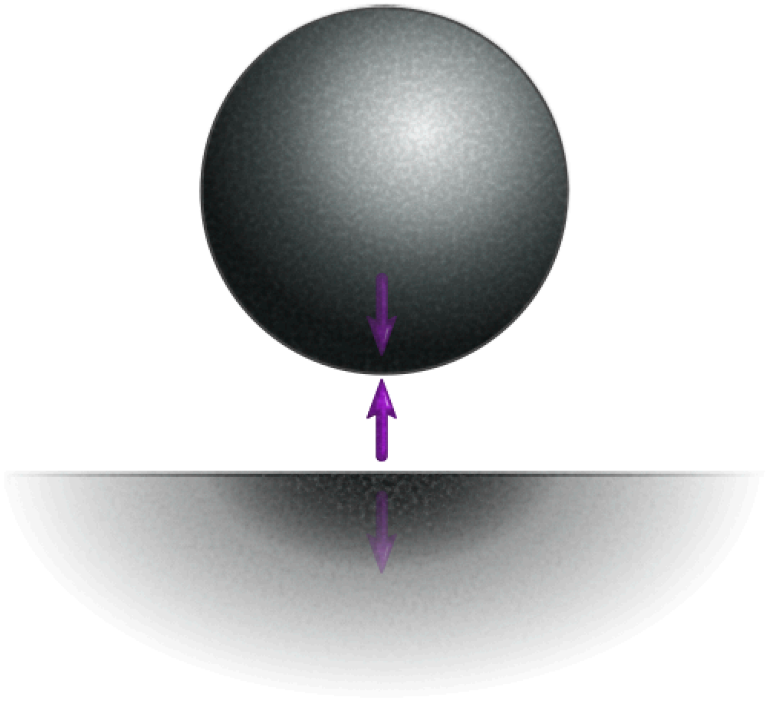
-all modes are important: Casimir-Polder $V_{eff}(\mathbf{R}) = V_0(\mathbf{R}) - \sum_k \frac{\lambda_k^2}{2}\left(\mu_o^2(\mathbf{R}) + \frac{\omega_k}{2}\alpha_0(\mathbf{R})\right)$

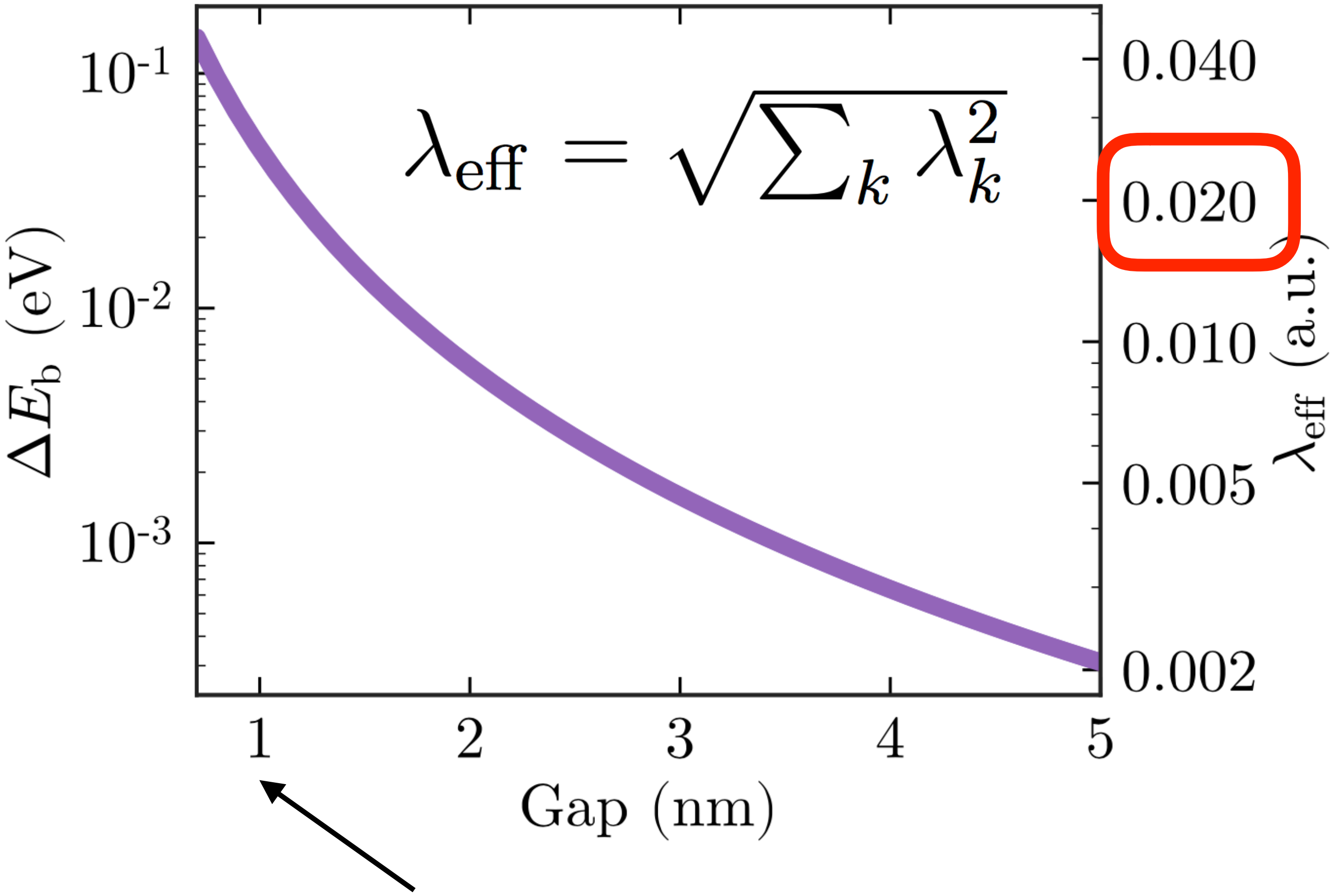
Different effect than in the experiments

Application to realistic systems

electrostatic problem (Debye) → energy shift → $\boldsymbol{\lambda}_{\mathrm{eff}}$

Nanoparticle-on-mirror cavity





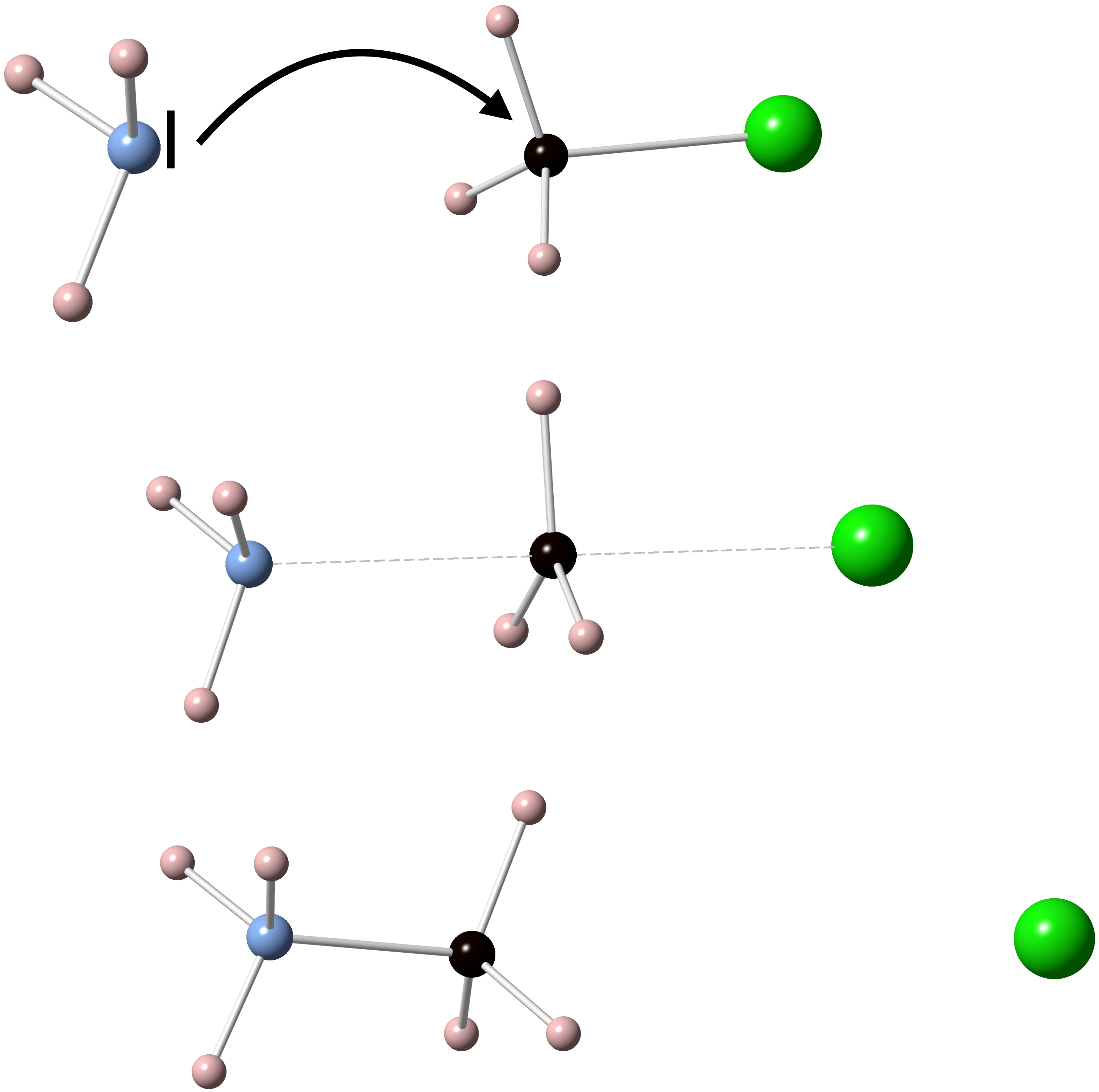
R. Chikkaraddy et al., "Single-molecule strong coupling at room temperature with plasmonic nanocavities", Nature 535, 127 (2016)

Significant single-molecule effects in experimentally available nanocavities

S_N2 reaction: Mechanism

(Nucleophilic Substitution)

N
C
Cl
H



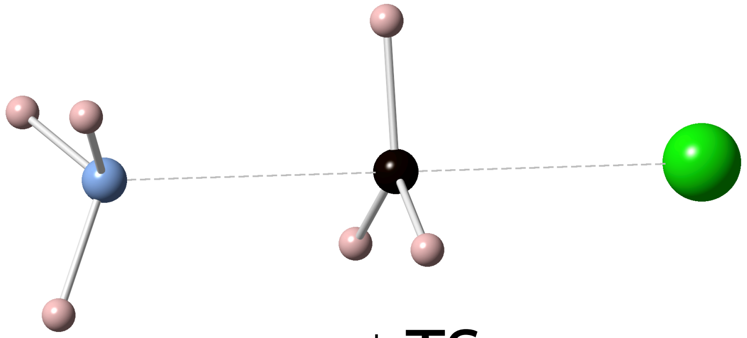
Reactants

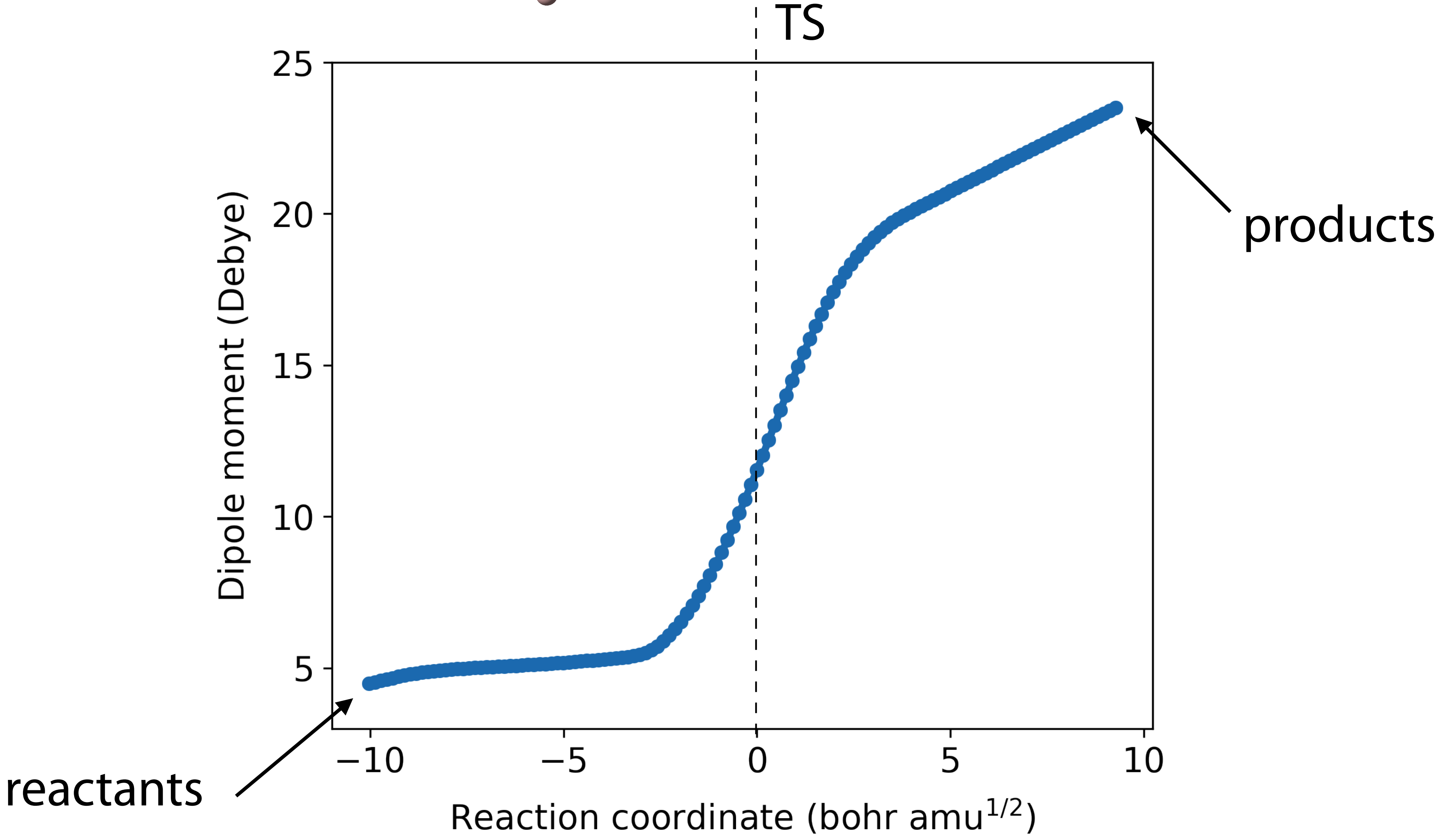
Transition State

Products

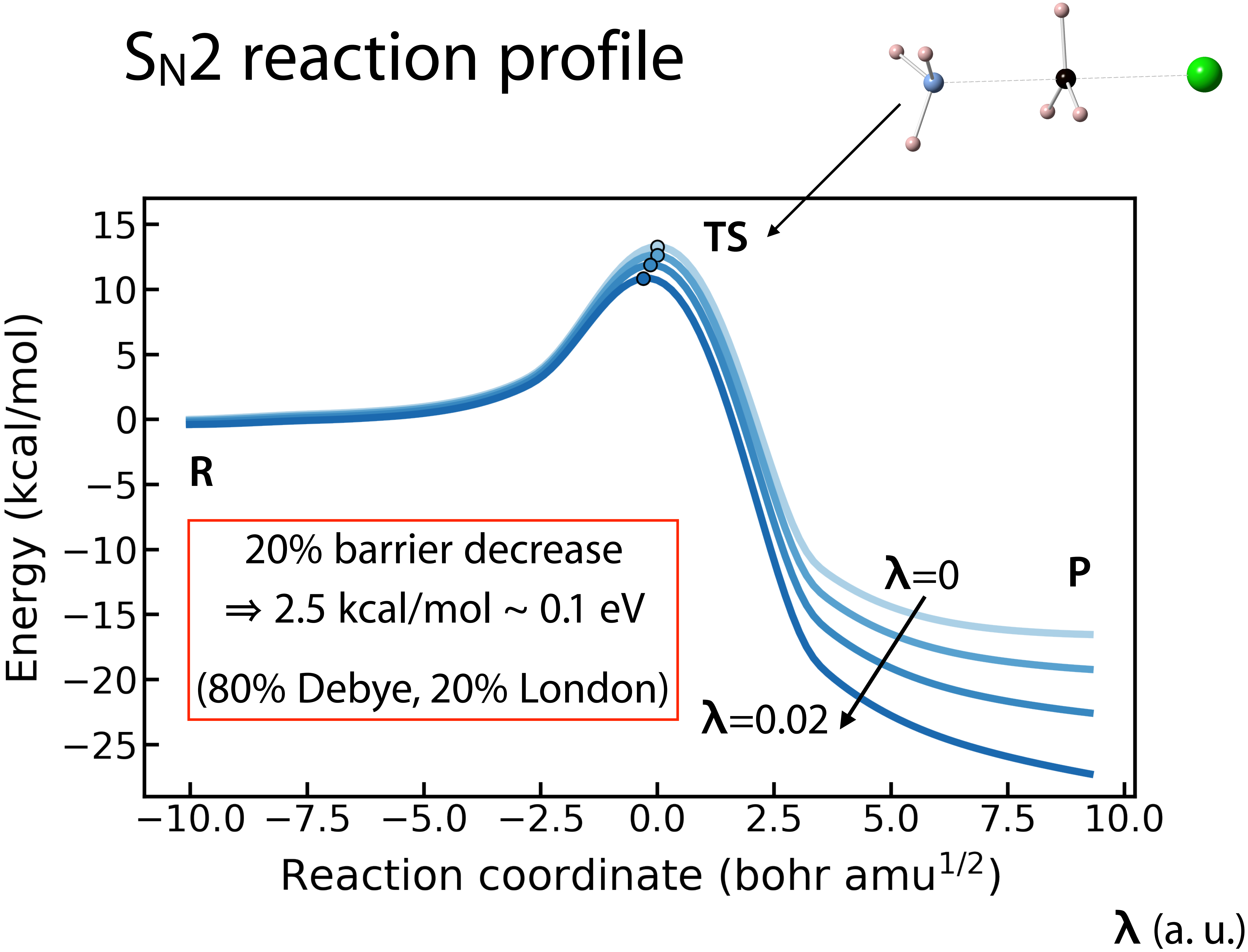
S_N2 reaction: μ profile

N
C
Cl
H





S_N2 reaction profile



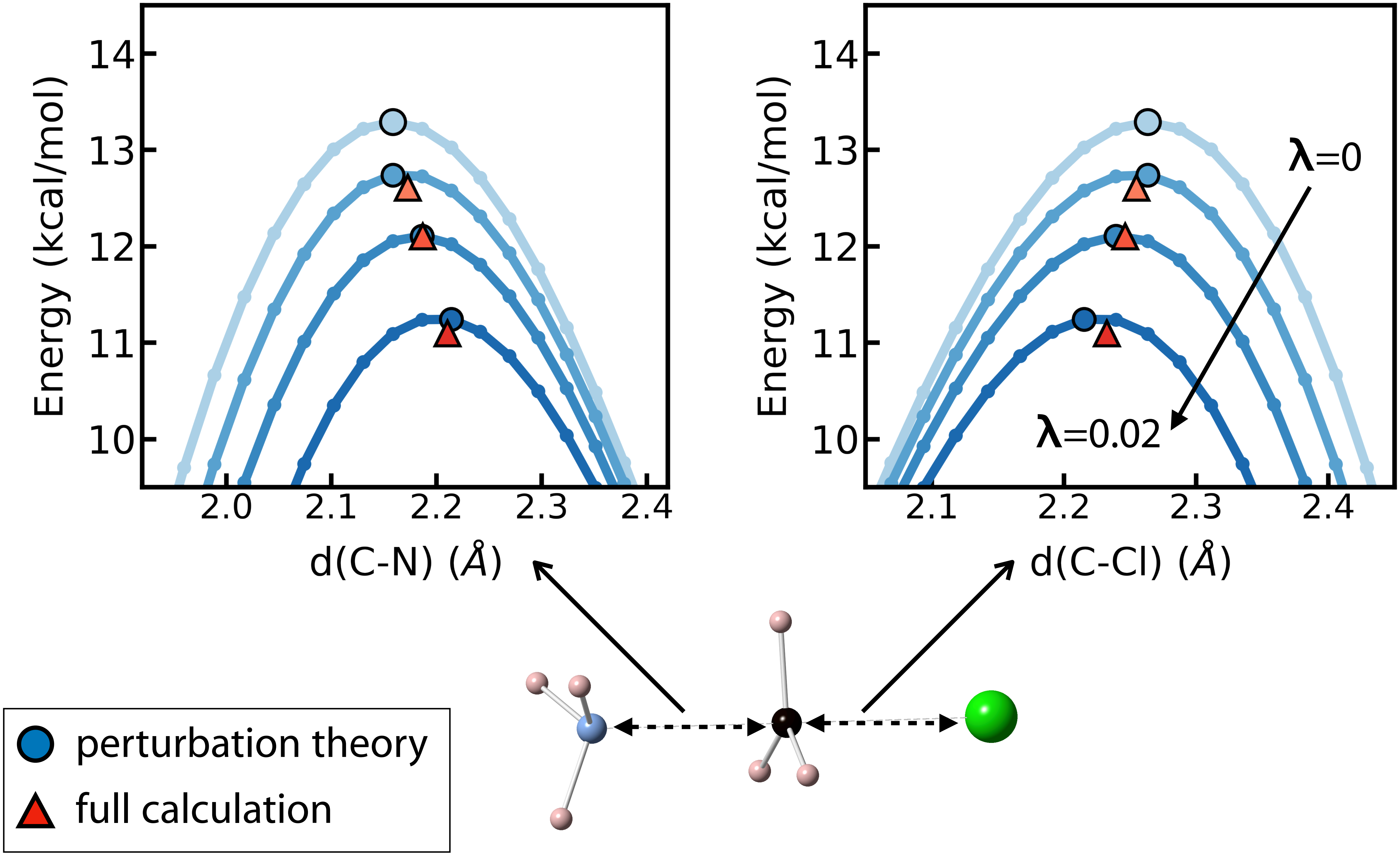
20% barrier decrease

⇒ 2.5 kcal/mol ~ 0.1 eV

(80% Debye, 20% London)

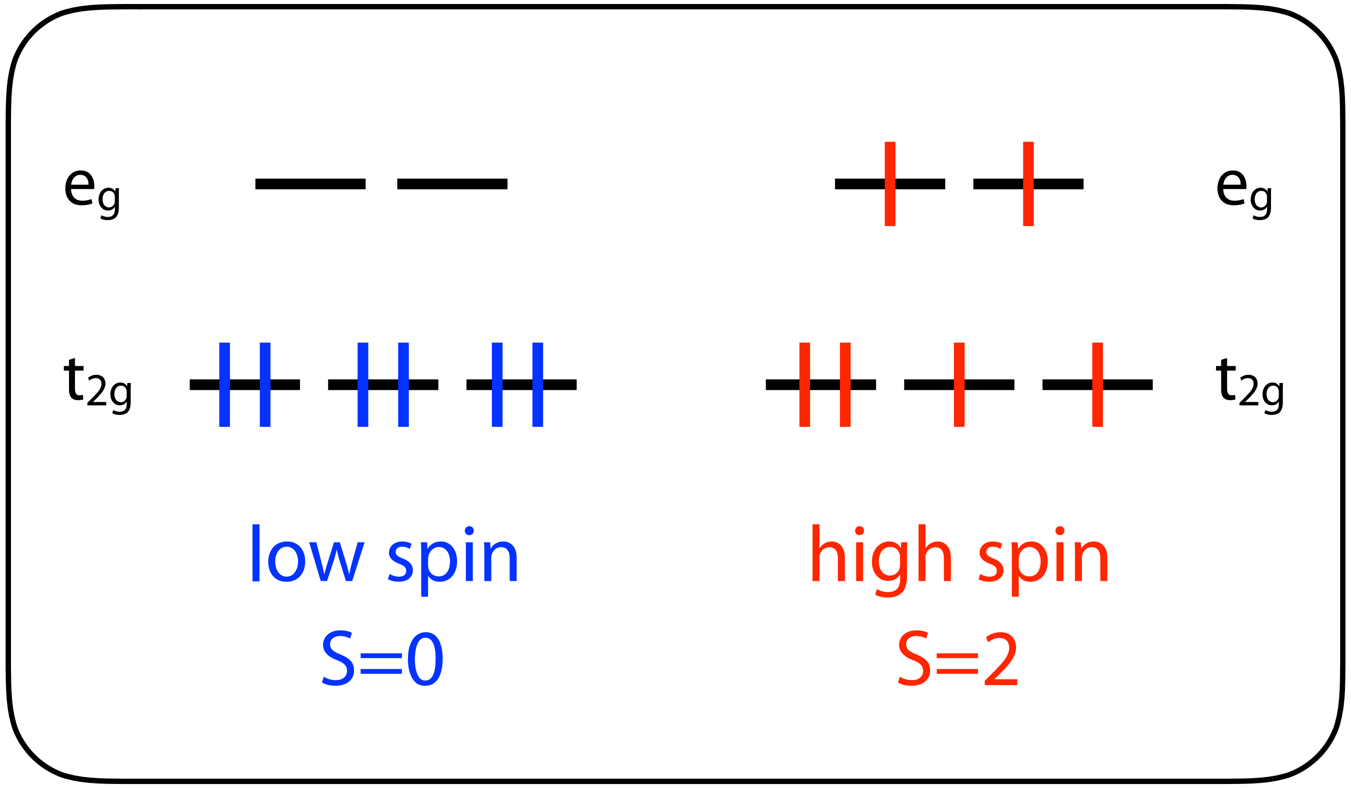
λ (a. u.)

S_N2 reaction: barrier region



Spin-crossover complexes

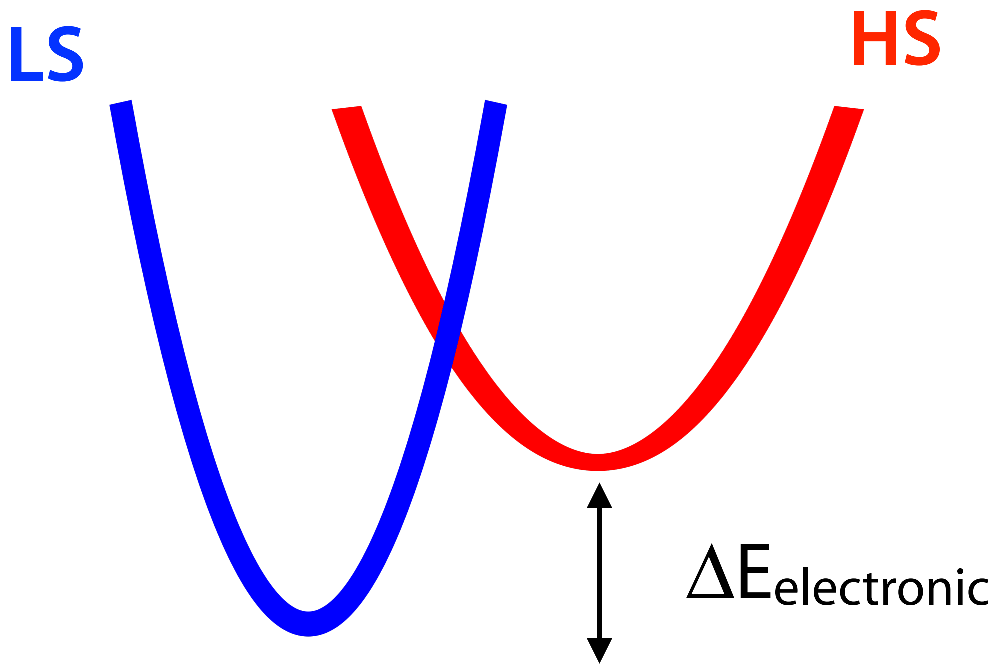
Fe(II) d⁶ (octahedral)

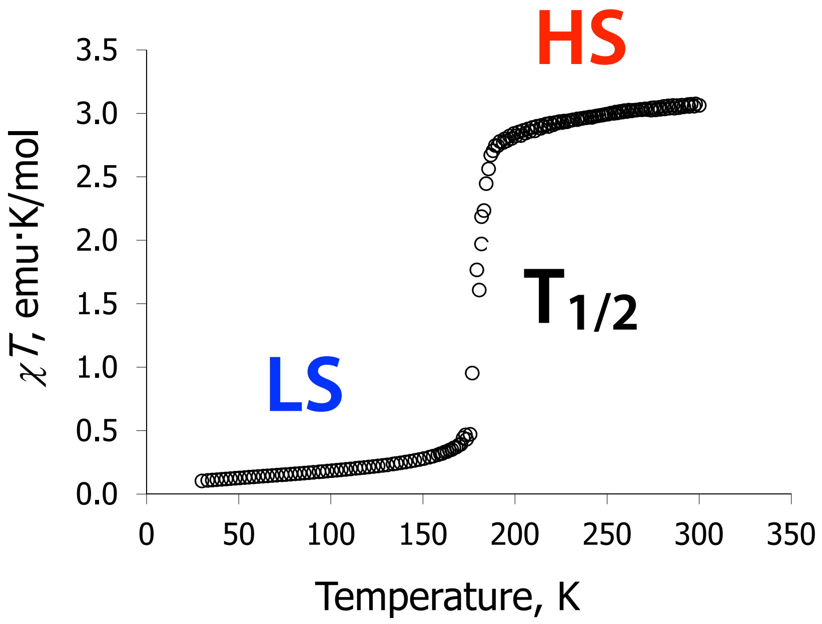


$$\Delta G = \Delta H - T\Delta S$$

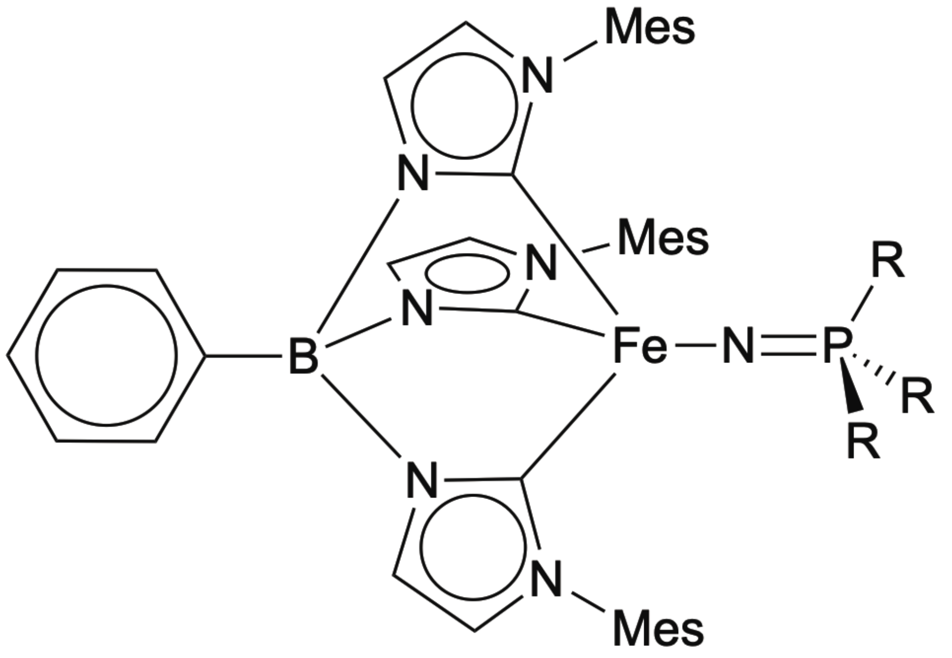
$$S_{electronic} = R\ln(2S+1)$$

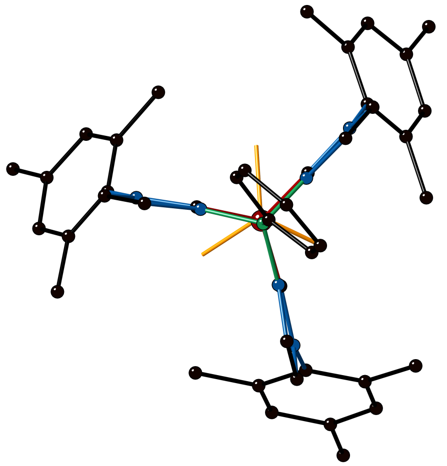
$$\Delta G(T_{1/2}) = 0$$

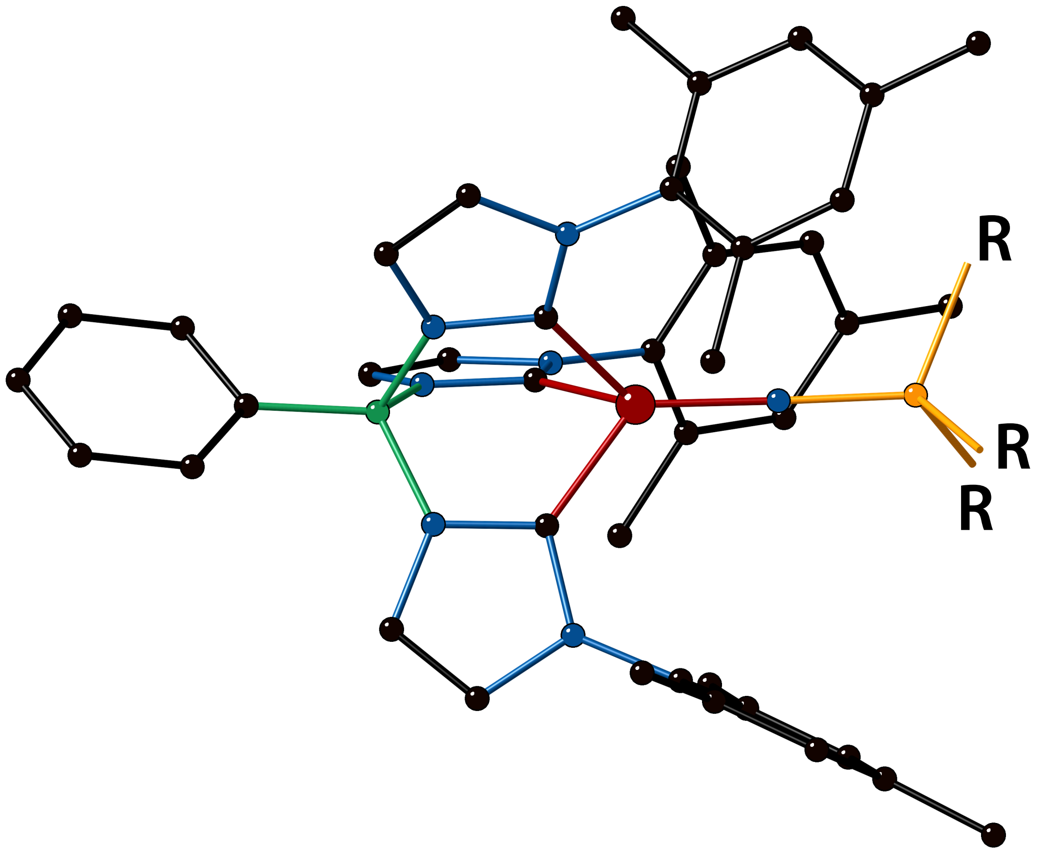




Spin-crossover complexes







		Experimental
	R	$T_{1/2}$ (K)
	H	-
CH_3	Me	340
$CH_2CH_2CH_3$	^{n}Pr	214
	Ph	81

E_{HS}-E_{LS} ~ 5 kcal/mol ~0.2 eV

$\mu_{LS} > \mu_{HS}$

H. J. Lin et al. , J. Am. Chem. Soc., 136, 13326 (2014)

SCO transition temperature $T_{1/2}$

R	Exp.	λ=0	λ=0.02	$\Delta T_{1/2}$
H	-	392	417	25
Me	340	351	384	33
^{n}Pr	214	192	226	34
Ph	81	74	98	24

J. Cirera, E. Ruiz, Inorg. Chem., 55, 1657 (2016)

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R	Exp.	$\lambda=0$	$\lambda=0.02$	$\Delta T_{1/2}$
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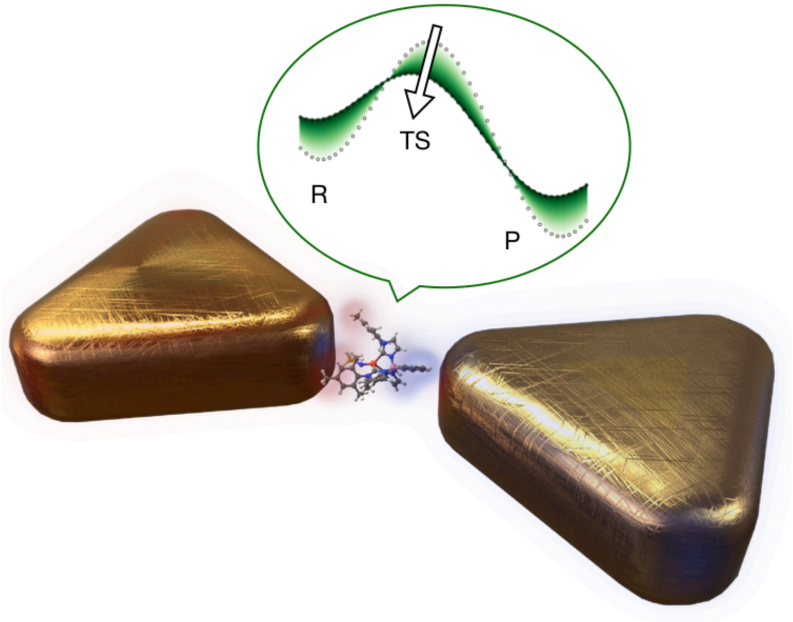
Final Remarks

-CBO + TST: ground-state chemical reactivity

-Connection to Casimir-Polder and Van der Waals interactions

-chemical reactivity / molecular properties



Cavity Casimir-Polder forces and their effects in ground state chemical reactivity
Phys. Rev. X 9, 021057 (2019)

Plasmonic Nanocavities Enable Self-Induced Electrostatic Catalysis
Angew. Chem. Int. Ed. 58, 8698 (2019)

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