LMU LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN

Quantum Dynamics of Diphenylmethylchloride in a Quasi-Diabatic Picture involving a three- and a two-state Conical Intersection in Quick Succession

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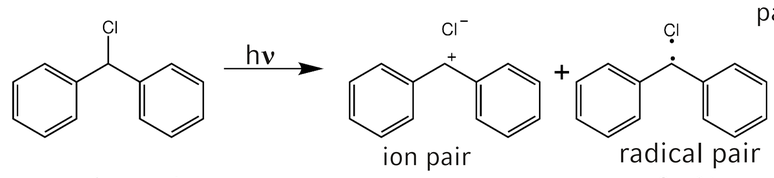
Abstract

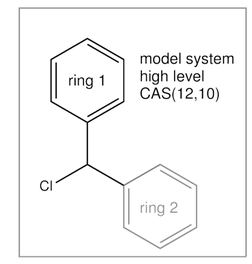
Carbocations and -radicals are well known reactive species both in organic synthesis and biochemistry. A convenient precursor for the photochemical generation of such intermediates is diphenylmethylchloride. We present a quantum dynamical description of this ultrafast reaction including all relevant conical intersections (CoIn) in a quasi-diabatic picture. In this description the computational cost is minimized by a succesful application of the ONIOM method and internal coordinates are used as reaction coordinates with the help of the G matrix approach. The three- and two-state CoIn coming in quick succession and acting as facilitators of the product splitting are optimized with standard quantum chemistry programs. The diabatization is based on the diagonalization of *ab initio* dipole moment and transition dipole moment data in the vicinity of the CoIn and the resulting electronic coupling elements are accounting for the non-adiabatic behaviour in this area. The now possible dynamics show qualitively similar results like the experiments.

Description of the Dissociation Process

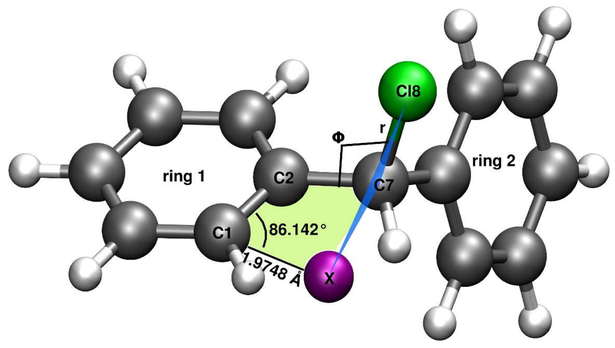


experimental quantum yield in acetonitril [1]:

ONIOM partitioning



real system
low level
DFT/B3LYP



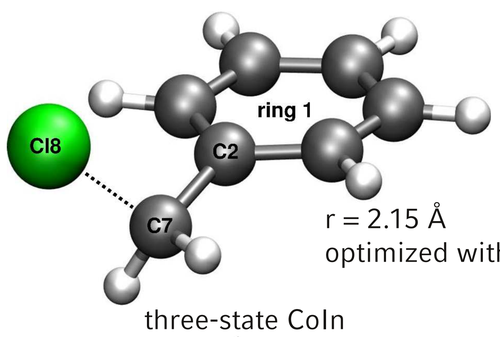
Main reaction coordinates: r, ϕ.
Relaxation around C7 is included via linear combination with r.

ONIOM (B3LYP/CAS(12,10))/6-31G*

$$\hat{H}_q = -\frac{\hbar^2}{2}\sum_{r=1}^{M}\sum_{s=1}^{M}\frac{\partial}{\partial q_r}\left[G_{rs}\frac{\partial}{\partial q_s}\right] + \hat{V}_q$$

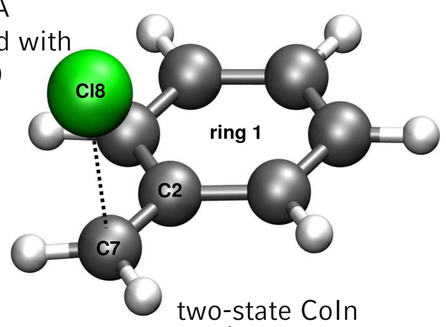
$$G_{rs} = \sum_{i=1}^{3N}\frac{1}{m_i}\frac{\partial q_r}{\partial x_i}\frac{\partial q_s}{\partial x_i} \qquad [2]$$

Relevant Conical Intersections (CoIn) & 1D Quasi-Diabatic PES



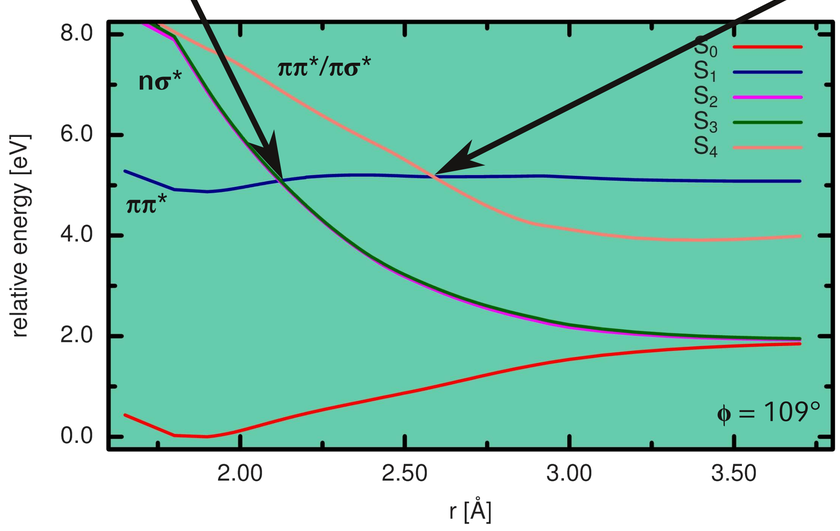
r = 2.15 Å
optimized with COLUMBUS

r = 2.58 Å
optimized with MOLPRO



three-state CoIn

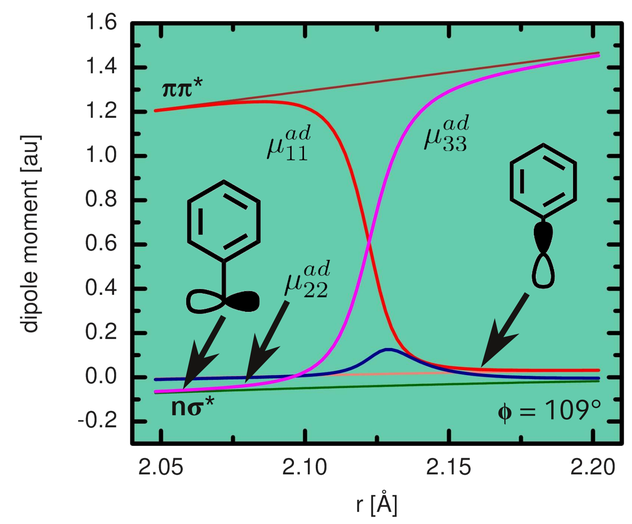
two-state CoIn



S_0-S_1 excitation energy: 4.87 eV/254 nm. Experimental value: 4.66 eV/266 nm [4].

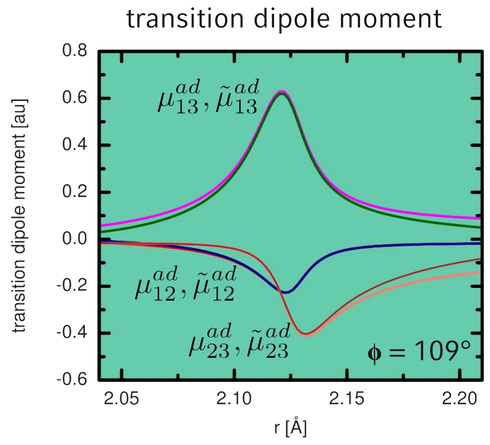
Diabatization via *ab initio* Dipole Moment Data

three-state CoIn



adiabatic vs. diabatic dipole moment

damped vs. undamped adiabatic transition dipole moment



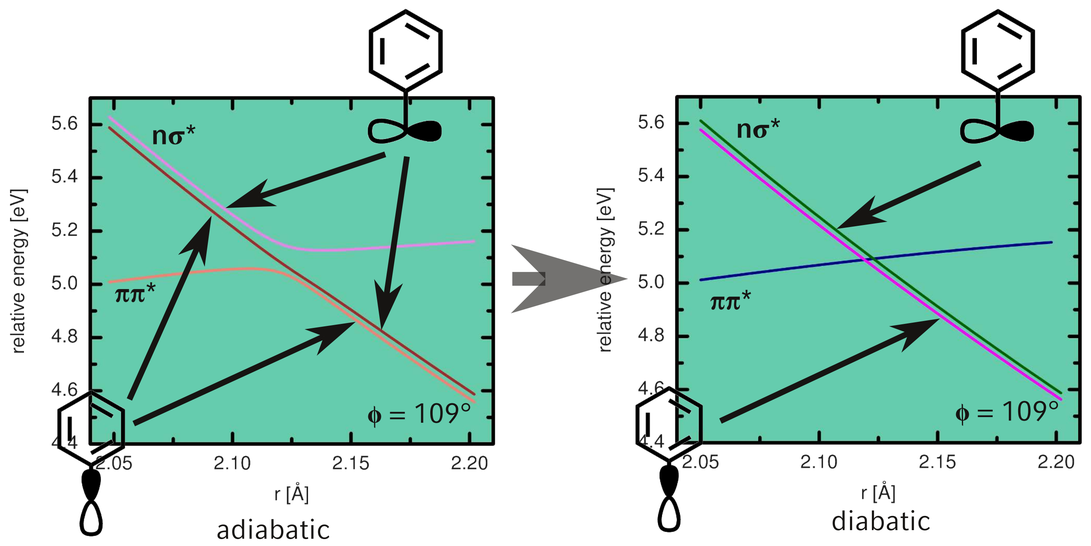
- Adiabatic dipole moment and transition dipole moment is projected in r direction.
- Off-diagonal terms are weighted according to the energy difference between states.
- Adiabatic dipole moment matrix is diagonalized -> transformation matrix U
- Adiabatic energies are transformed using U

$$\Psi_i^{dia} = \sum_k \Psi_k^{ad} U_{ki}$$

$$\tilde{\mu}_{ij}^{ad} = \mu_{ij}^{ad} \cdot e^{-f\Delta E_{ij}^2}$$

$$\boldsymbol{\mu}^{ad} = \mathbf{U}\boldsymbol{\mu}^{dia}\mathbf{U}^{\dagger}$$

$$H_{ij}^{dia} = \sum_k U_{ki} E_k U_{kj} \qquad [5]$$



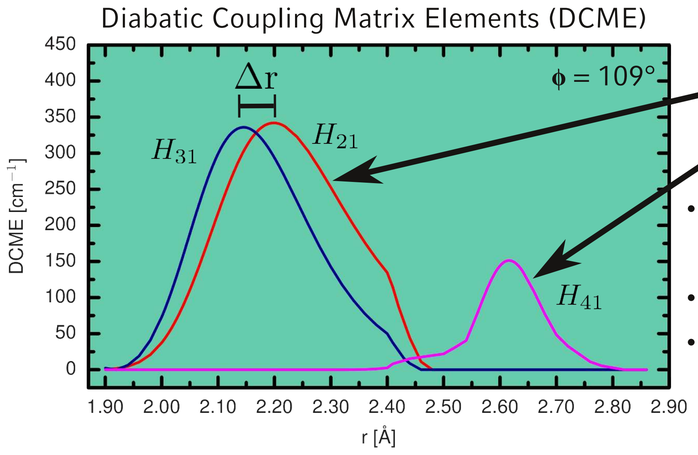
1D Dynamics

$$\hat{H} = \begin{pmatrix} \hat{T}_{nuc} & 0 & 0 & 0 & 0 \\ 0 & \hat{T}_{nuc} & 0 & 0 & 0 \\ 0 & 0 & \hat{T}_{nuc} & 0 & 0 \\ 0 & 0 & 0 & \hat{T}_{nuc} & 0 \\ 0 & 0 & 0 & 0 & \hat{T}_{nuc} \end{pmatrix} + \begin{pmatrix} H_{00} & -\epsilon(t)\hat{\mu}_{01} & 0 & 0 & 0 \\ -\epsilon(t)\hat{\mu}_{01} & H_{11} & H_{12} & H_{13} & H_{14} \\ 0 & H_{21} & H_{22} & 0 & 0 \\ 0 & H_{31} & 0 & H_{33} & 0 \\ 0 & H_{41} & 0 & 0 & H_{44} \end{pmatrix}$$

coupling between the lone pairs is ignored!

ππ*/πσ*

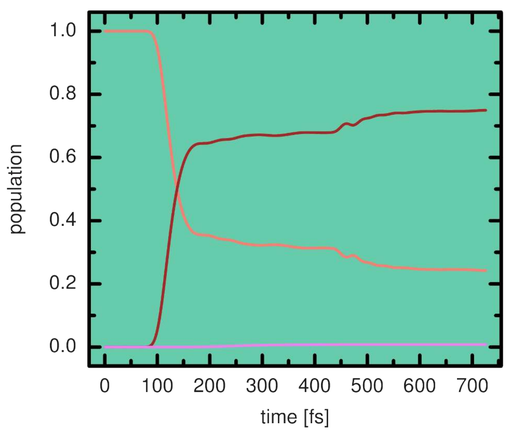
Diabatic Coupling Matrix Elements (DCME)



three-state CoIn couplings

two-state CoIn coupling

- Three-state CoIn couplings 2x larger than two-state CoIn coupling
- Both lone pair channels equal
- Δr results from different transition dipole moment maxima



$Ph_2CH^{\bullet}$ $Cl^{\bullet}$ 75 %

$Ph_2CH^{\bullet *}$ $Cl^{\bullet}$ 24 %

Ph_2CH^{+} Cl^{-} 1 %

coupling into ionic channel very weak!

- Successful population transfer into the lone pair states
- Qualitatively similar results like in the experiments
- Confirmation of the reaction mechanism

Outlook

- Interpolation of the DCME for various angles ϕ and dynamics in 2D
- Tests with other second coordinates
- Inclusion of simulated solvent effects
- Time dependent relaxation
- Simulation of similar molecules like diphenylmethylbromide

References

[1] C.F. Sailer, S. Thallmair, B.P. Fingerhut, C. Nolte, J. Ammer *et al.*, *ChemPhysChem* **14**, 1423 (2013).

[2] E.B. Wilson, J.C. Decius, P.C. Cross, *Molecular Vibrations*, Dover, New York, NY (1980). L. Schaad, J. Hu, *J. Mol. Struct.: THEOCHEM* **185**, 203 (1989); M. Kowalewski, *Doktorarbeit*, LMU München (2012).

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