Theoretical Modelling of the Photodynamical Processes in 2-Enones: Towards Time-Resolved Signals in Explicit Solvents

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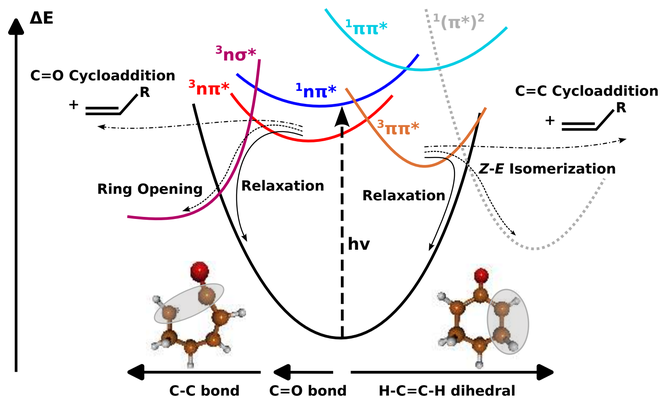
Diverse Photoreaction and Relaxation Pathways in 2-Enones

Goal: Understand the diverse photoreactivity of (cyclic) 2-enones and how it is influenced by Lewis acid photocatalysts

nπ* Reactivity
Paternò-Büchi reaction
α-cleavage (ringsize < 6) [2]

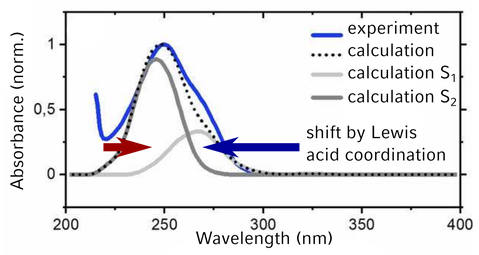
ππ* Reactivity
[2+2]-cycloaddition
Z/*E*-isomerization (ringsize > 6) [3]

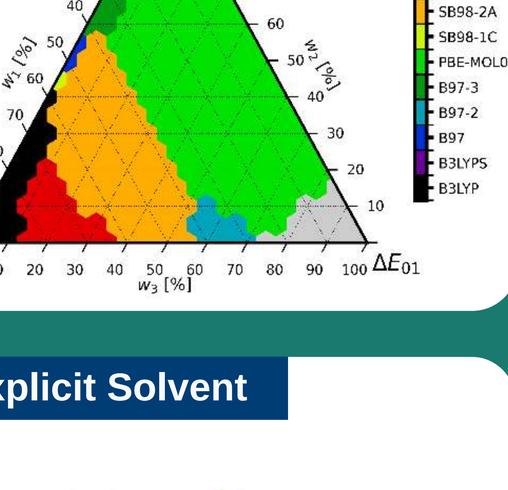


The Influence of Lewis Acids on the Excited States

- low-lying π* due to −M effect of the carbonyl group
- −M effect enhanced by Lewis acid coordination
- dative bond to Lewis acid lowers n-orbital
- blueshift of nπ*, redshift of ππ* states
  - → effective photocatalysts [4,5]

UV-Vis Spectrum of Cyclohexenone-BF_3

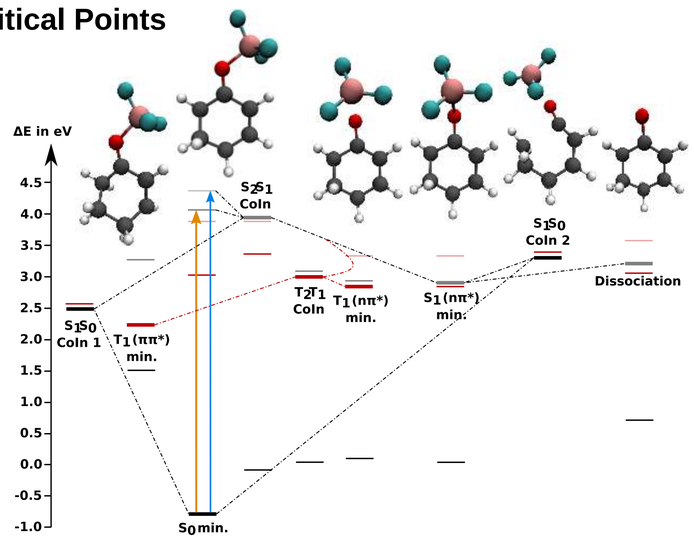




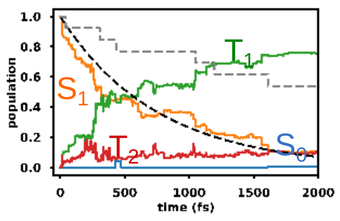
Surface Hopping Dynamics of Cyclohex-2-enone and its BF_3 Complex in the Gas Phase [1]

Methods
augmented FSSH using SHARC [6]
Gradients: XMS-CASPT2(8,7)/cc-pvdz by BAGEL [7]
Spin-Orbit Couplings: RASSI by OpenMOLCAS [8]

Critical Points

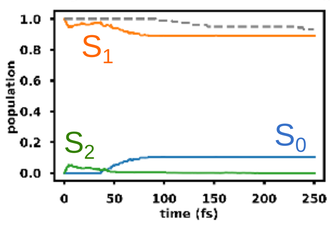


Cyclohexenone



Relaxation to T_1 (τ = 750 fs) via $^1n\pi^* \rightarrow {}^3n\pi^* \rightarrow {}^3\pi\pi^*$

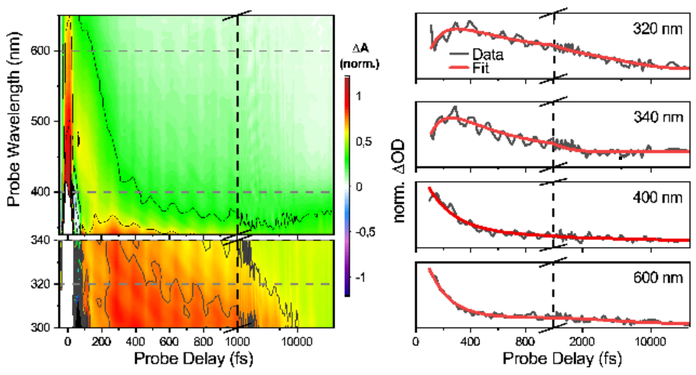
Cyclohexenone-BF_3



Ultrafast Dissociation of the Lewis acid in $S_1(n\pi^*)$ with 10% Relaxation to S_0

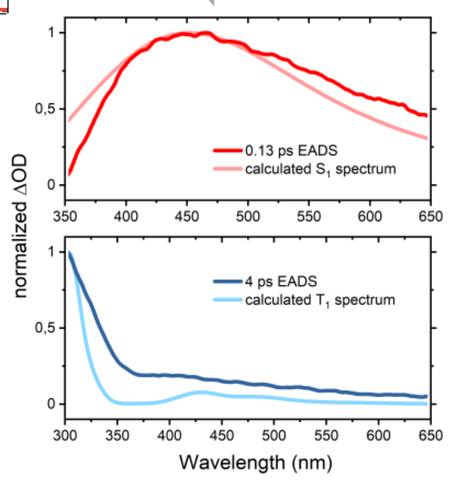
Ultrafast Transient Absorption Measurements, Kinetic Model and Relaxation Timescales [1]

Pump: 285 nm, excitation predominantly to S_1



No stimulated emission
Excited state absorption shifts from ~450 nm into the UV

Kinetic Modelling
A → B → C → ...



4 ps EADS matches the spectrum of the complex in $T_1(\pi\pi^*)$

Blueshift would be much smaller in case of dissociation

→ Relaxation to $T_1(\pi\pi^*)$ with the Lewis acid attached

The evolution-associated decay spectra (EADS) can be directly compared to XMS-CASPT2 spectra calculated at and around critical points using Wigner sampling.

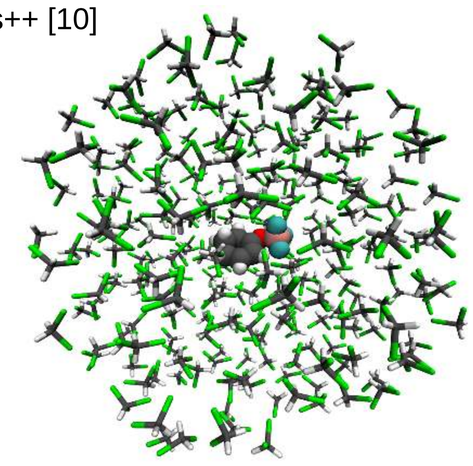
Benchmarking TDDFT Functionals

- Extensive benchmark of 93 functionals in LibXC [9]
- Tested on random points of the trajectories
- Reference: XMS-CASPT2(6,5)/cc-pvqz
- Evaluation criteria:
  - S_1 gradient ...∇E_1
  - S_1/S_0 energy gap ...ΔE_{01}
  - S_1/S_2 energy gap ...ΔE_{12}
- Measure of Error: weighted sum of normalized RMSDs

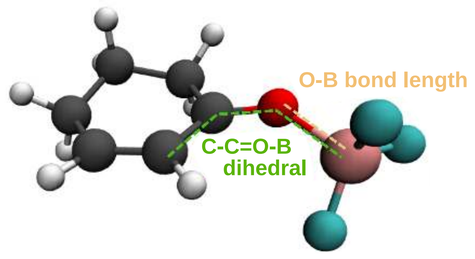
Functionals with minimal measure of error for different weights of the evaluation criteria

Surface Hopping Dynamics in an Explicit Solvent

Methods
Gradients QM: TDA-PBE-MOL0 using FermiONs++ [10]
Gradients MM: OPLS/AA
Wavefunction Overlaps: cis_nto [11]
so far: Singlets only

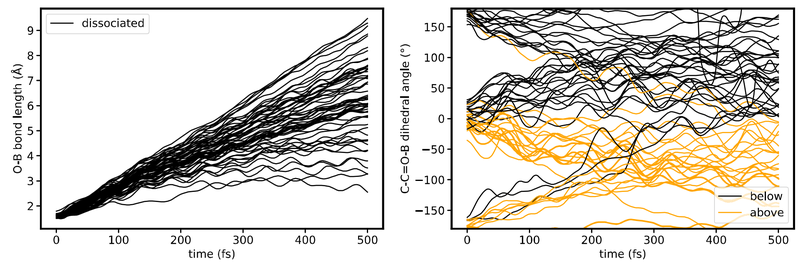


System
Cyclohexenone-BF_3 surrounded by 268 molecules of dichloromethane in a 20 Å sphere



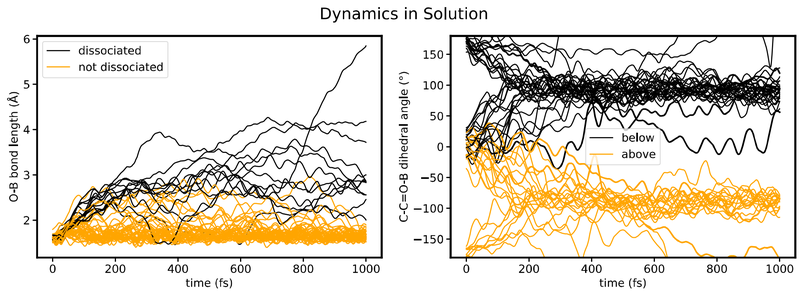
Coordinates
O-B bond length: Dissociation
C-C=O-B dihedral: Relaxation in S_1

Gasphase Dynamics



Gasphase
Rapid dissociation in all trajectories, no preferential orientation of dihedral angle

Dynamics in Solution



Solution
Dissociation prevented in most trajectories, 90°/−90° preferential orientation of the dihedral, BF_3 moves above or below the molecular plane

Solvation prevents ultrafast dissociation and vibrationally cools the complex such that relaxation to shallow minima becomes possible.

References

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