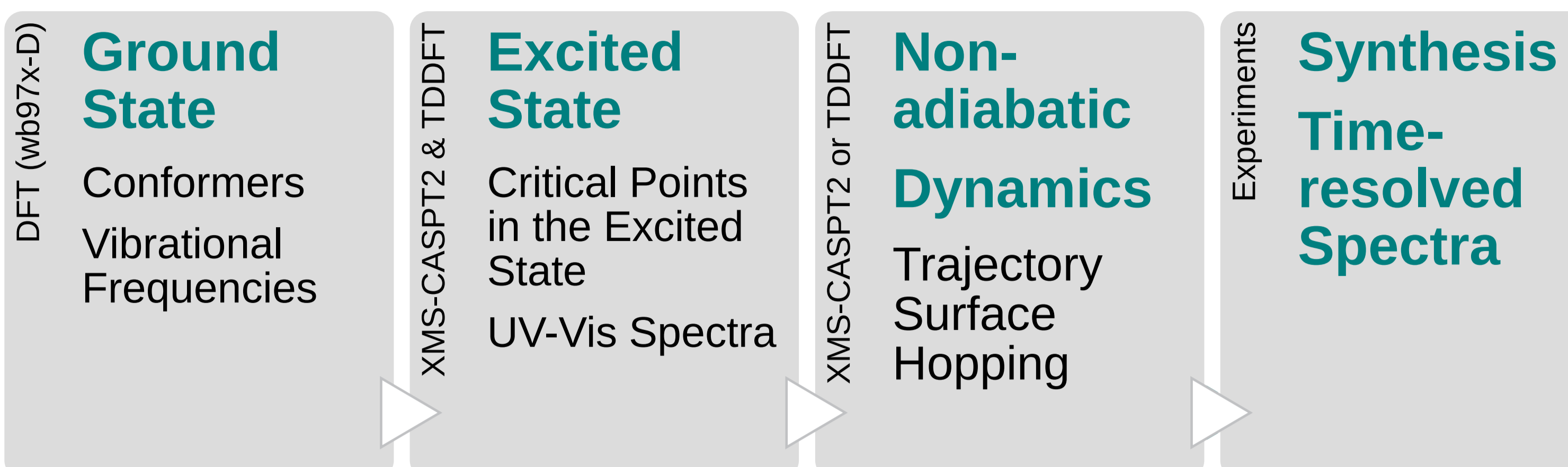


ABSTRACT

α,β -Enones serve as important building blocks in synthetic organic chemistry. Their excited state reactivity is highly dependent on their specific structure[1] and on the coordination environment of the carbonyl oxygen.[2,3] To better understand how Lewis acids steer the photochemical reactions of these compounds, we investigate two exemplary complexes, cyclohexenone- BF_3 and benzaldehyde- BCl_3 . Our multidisciplinary study employs nonadiabatic dynamics (augmented fewest switches surface hopping[4,5]) at a high level of electronic structure theory (XMS-CASPT2, TDDFT), femtosecond UV/Vis transient absorption and organic synthesis. The examples demonstrate the potential of *in silico*-guided photochemical studies and the predictive power of modern quantum chemistry for both photochemical reactivity and spectroscopic properties.

WORKFLOW

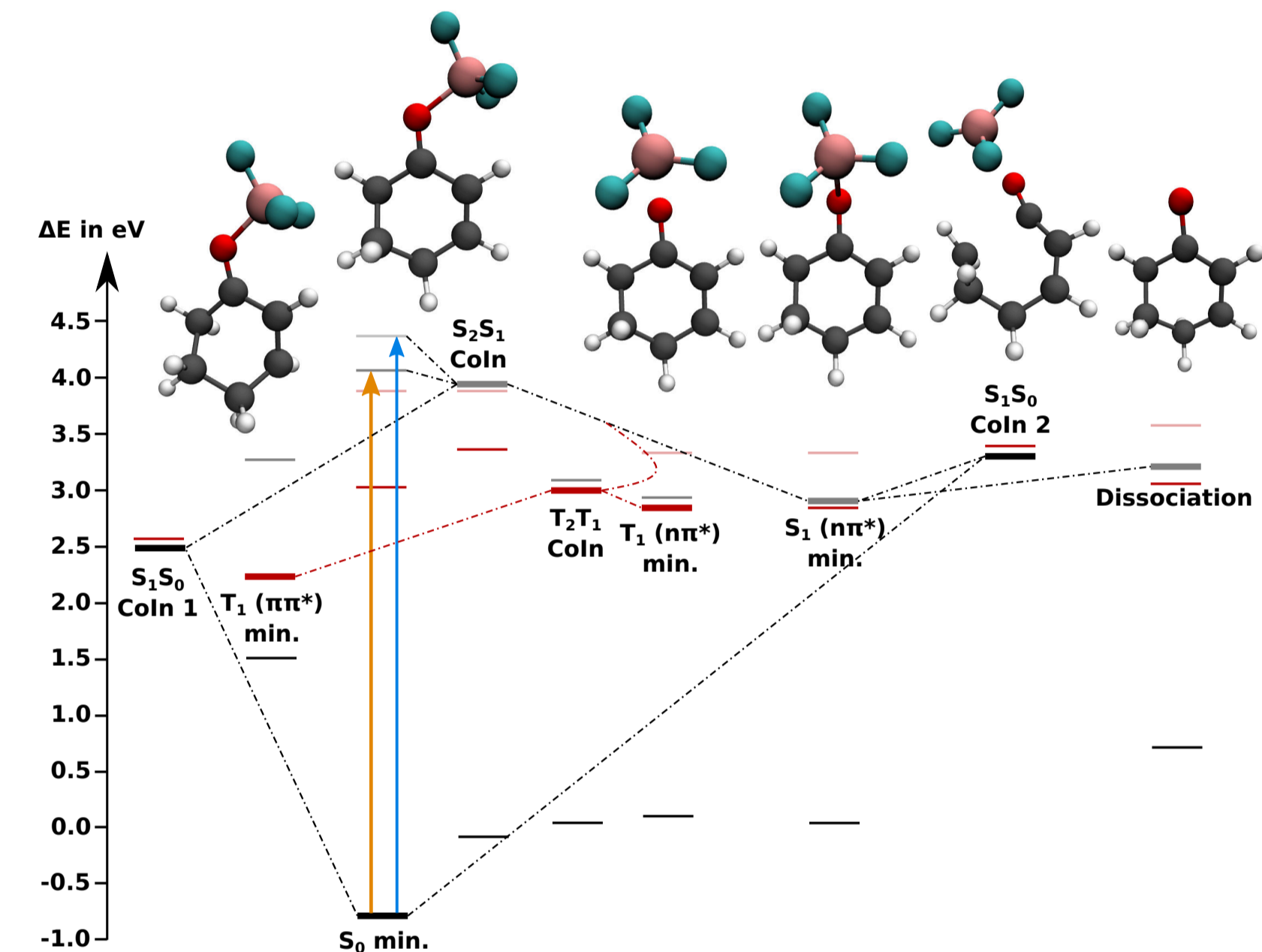


CYCLOHEXENONE- BF_3

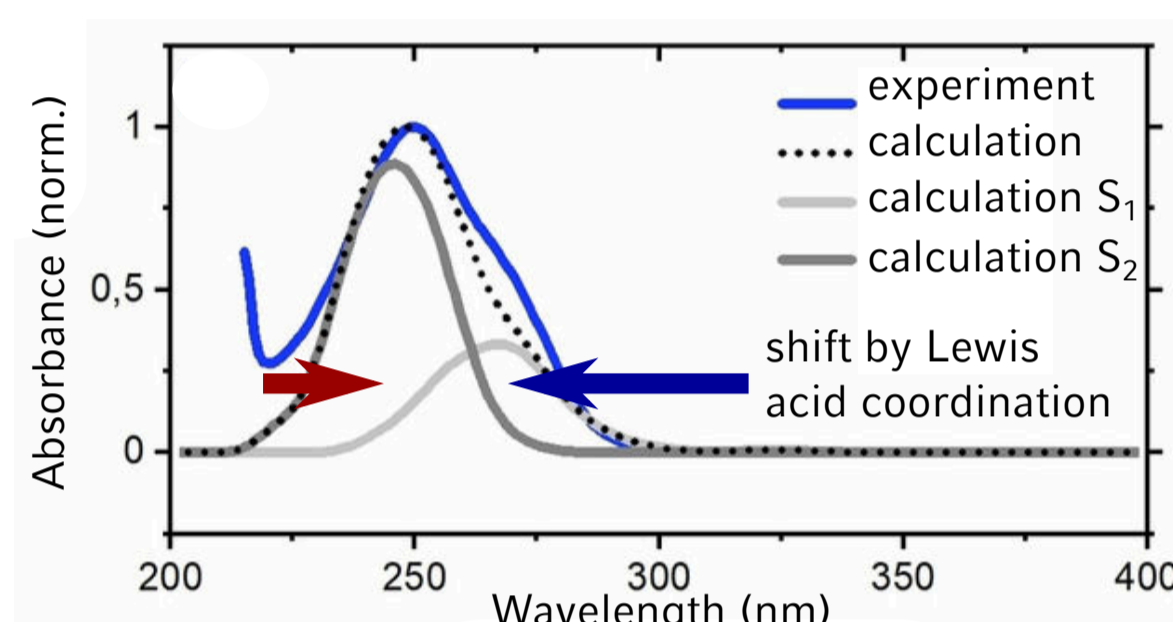
Activation of the Enone by the Lewis Acid

Electronic Structure Method:
static calculations: XMS-CASPT2(6,5)/cc-pvtz
dynamic calculations: XMS-CASPT2(8,7)/cc-pvdz

Critical Points [3]



UV-Vis Spectrum of Cyclohexenone- BF_3 [3]

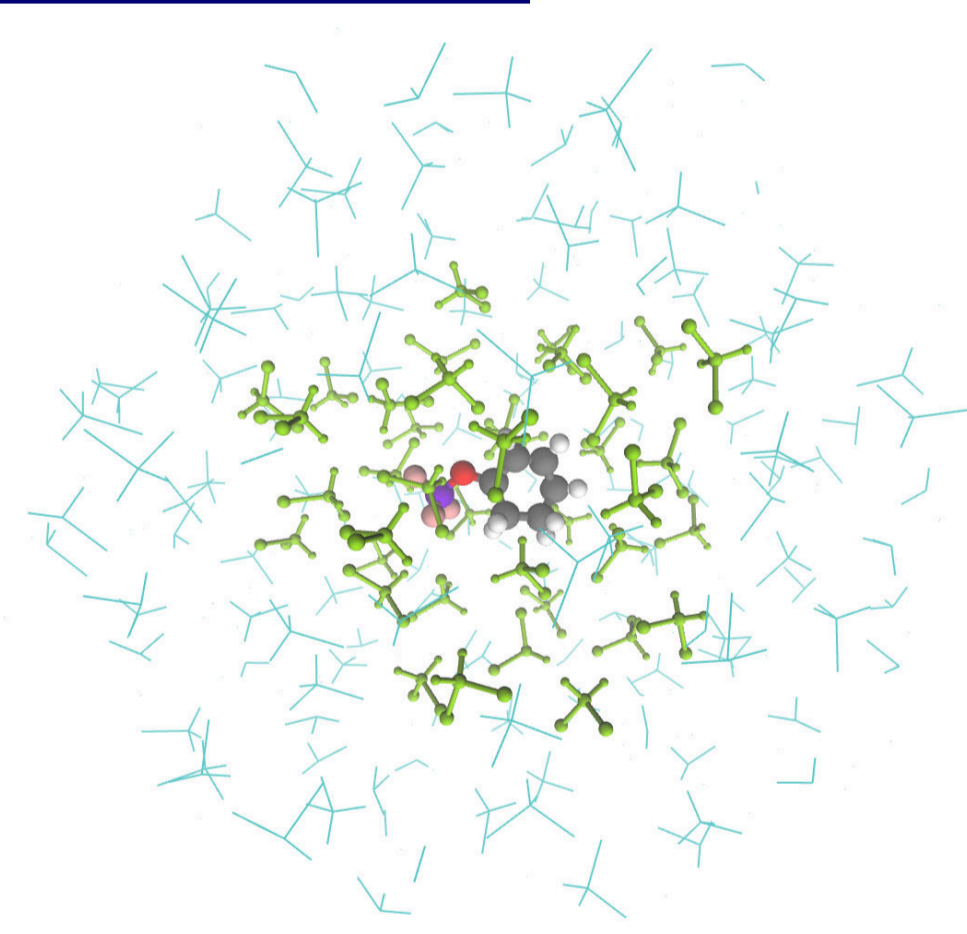


Coordination of the Lewis acid strongly stabilizes HOMO (n_0) and weakly stabilizes LUMO (π^*) leading to a blueshift of $S_1(n_0\pi^*)$ and a redshift of $S_2(\pi\pi^*)$

Surface hopping dynamics in the singlets states shows dissociation of the Lewis acid in the gas phase

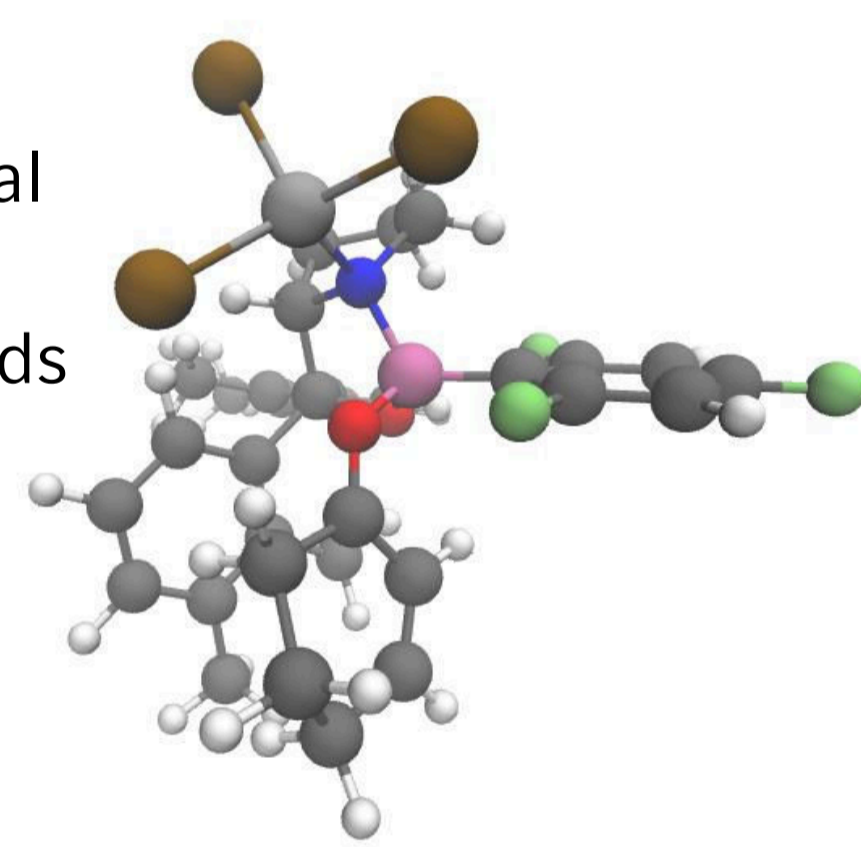
Apparent contradiction with experiment (see below), dynamic solvent effects? influence of the triplet states?

OUTLOOK



Investigation of large, chiral Lewis acid photocatalysts using linear scaling methods

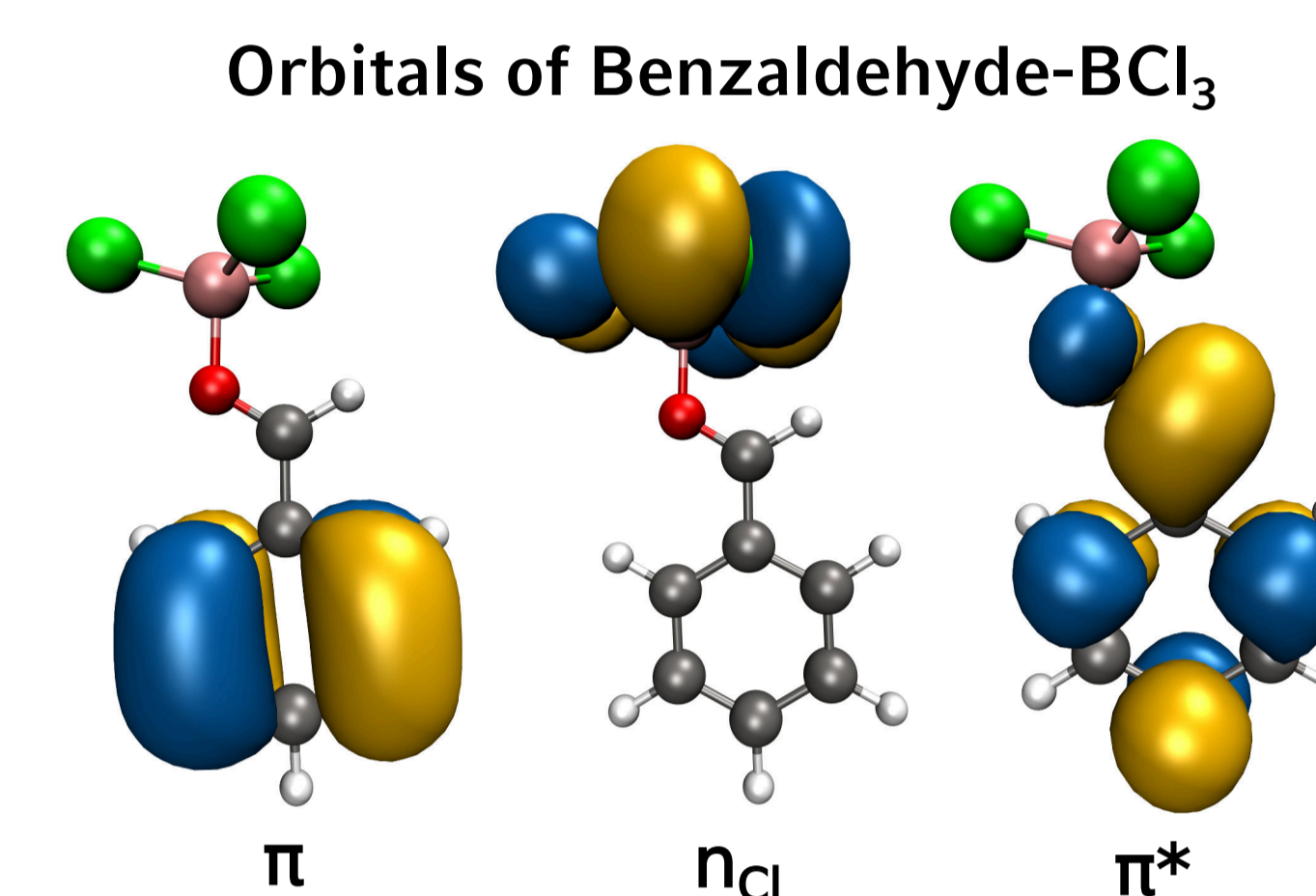
Dynamics in explicit solvent environments using QM/MM embedding



BENZALDEHYDE- BCl_3

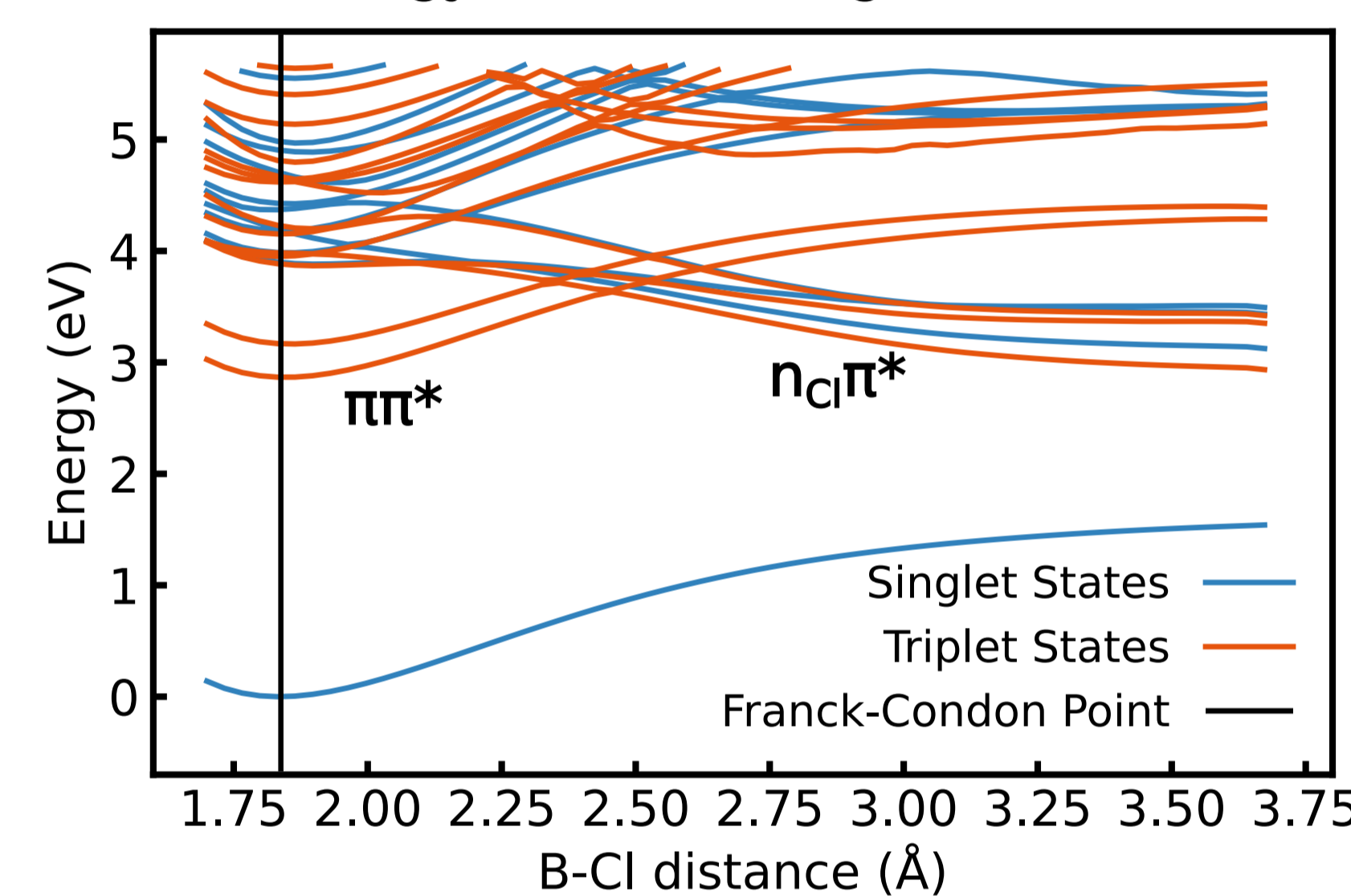
Activation of the Lewis Acid by the Enone

Electronic Structure Method:
scaled TD-wB97x-D3/def2-TZVP,
scaling benchmarked using
XMS-CASPT2(18,14)/ANO-RCC-VTZP



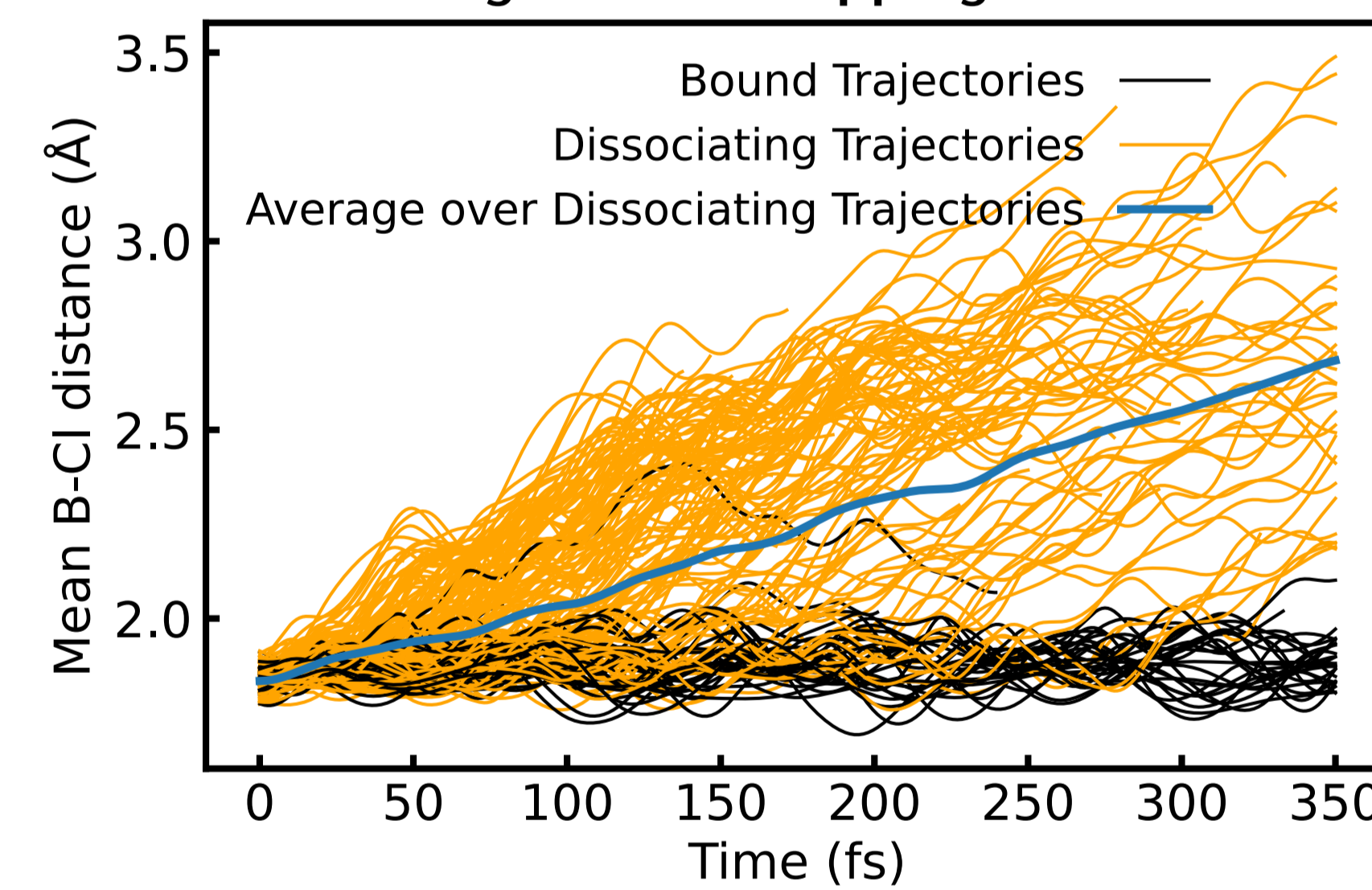
Complex excited state structure due to the involvement of multiple $n_{Cl}\pi^*$ charge transfer states of both singlet and triplet character

Potential energy surfaces along B-Cl bond stretch [6]



Crossings between $\pi\pi^*$ and $n_{Cl}\pi^*$ in the Franck-Condon region mediate transfer of an electron from chlorine into the aromatic system

B-Cl Bond Distances During Surface Hopping Simulation [6]



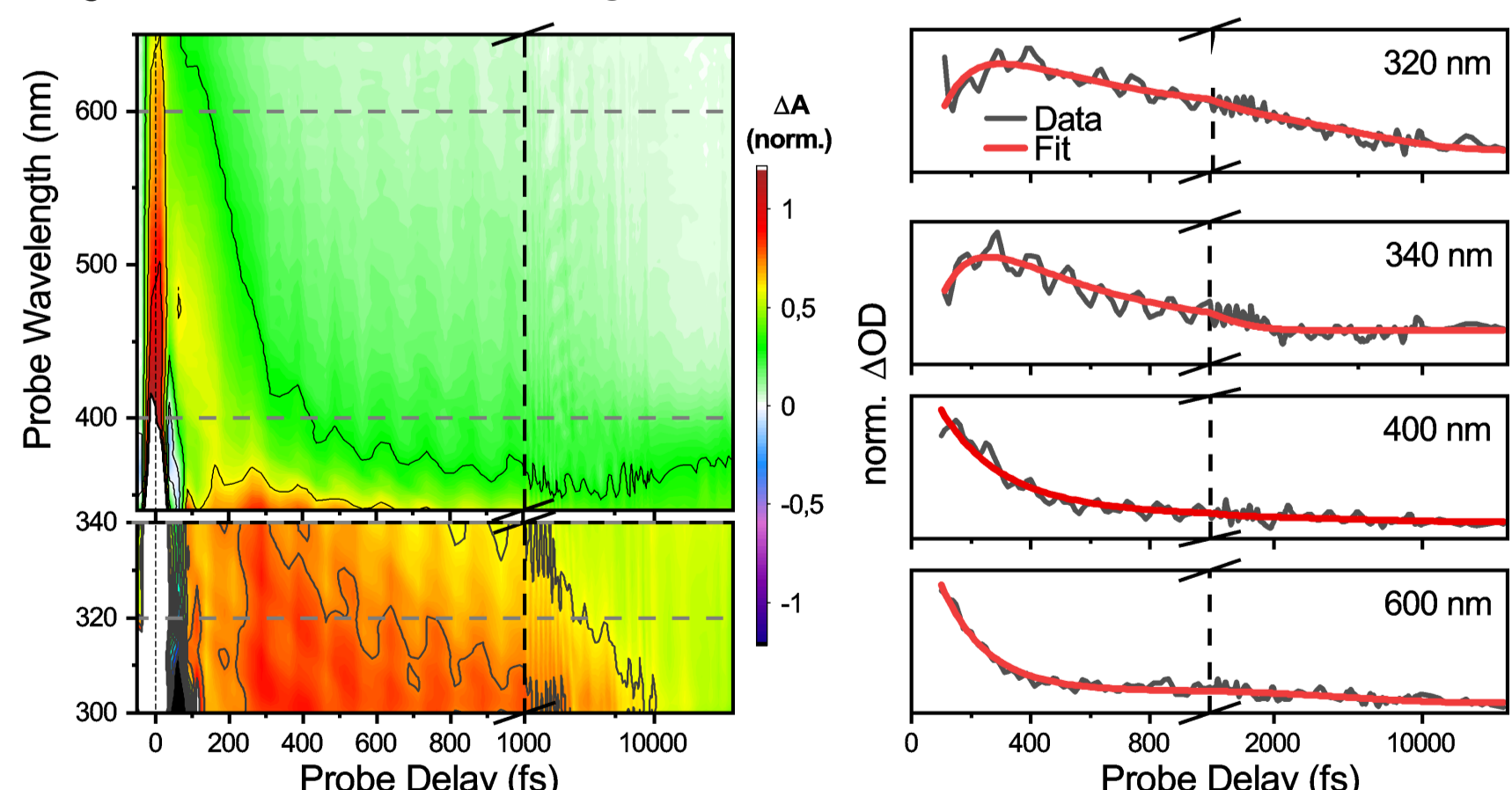
Surface hopping dynamics shows dissociation of a chlorine radical on ultrafast timescales

Chlorine radical can be employed in hydrogen atom transfer reactions

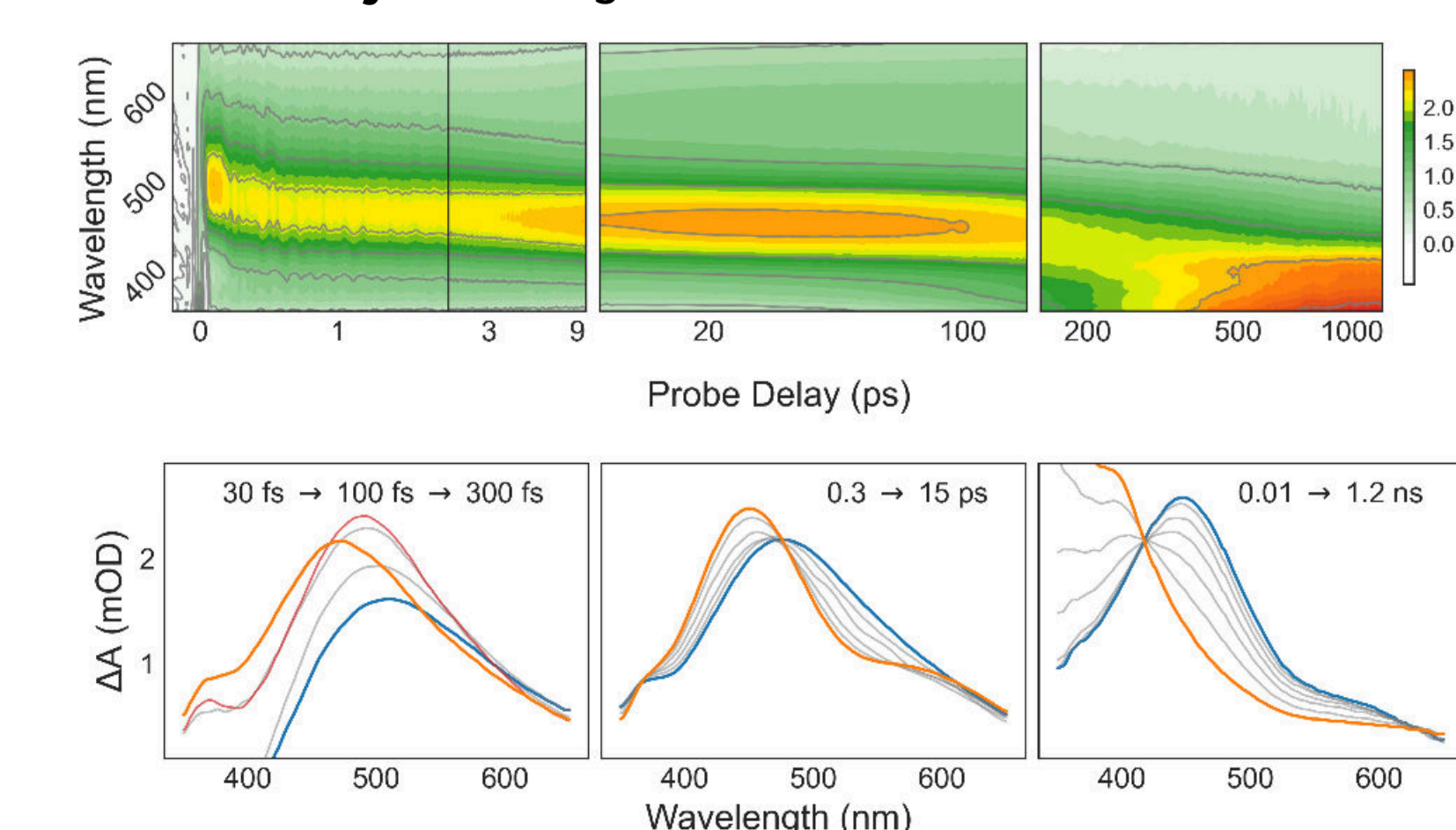
UV-VIS TRANSIENT ABSORPTION

Experiments + Global Kinetic Fits

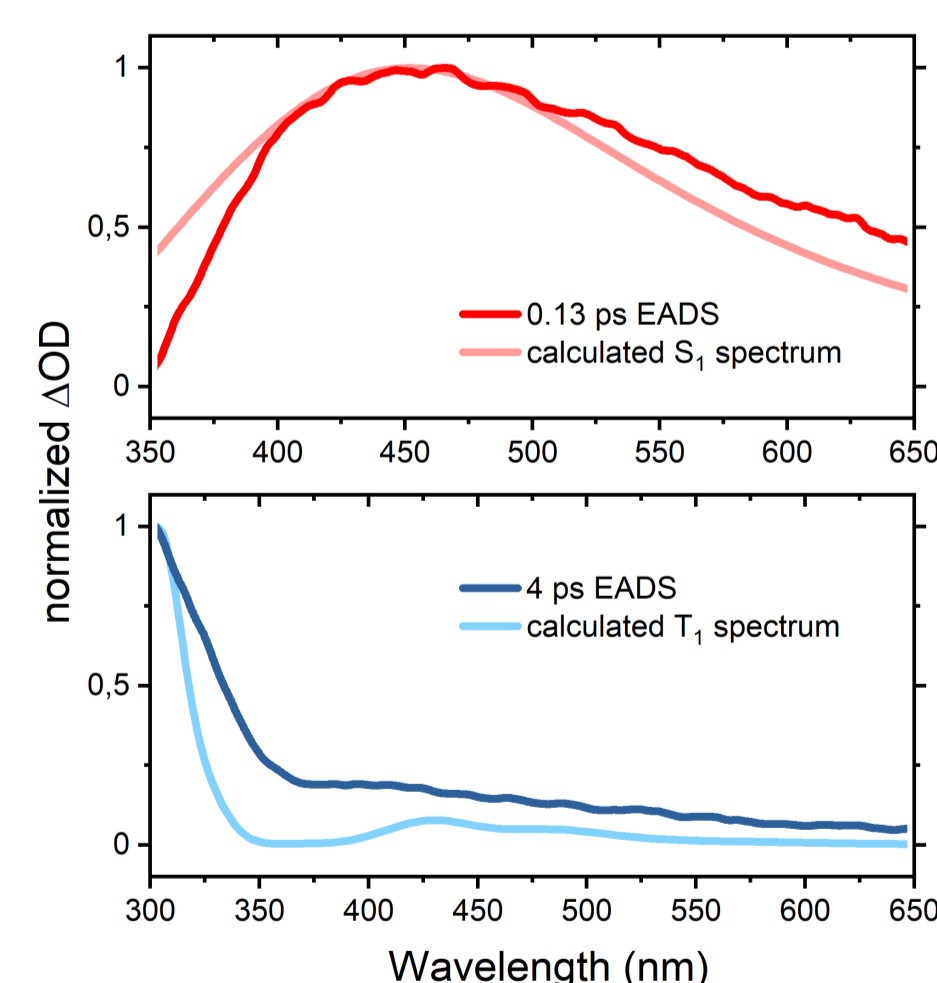
Cyclohexenone- BF_3 [3]



Benzaldehyde- BCl_3 [6]



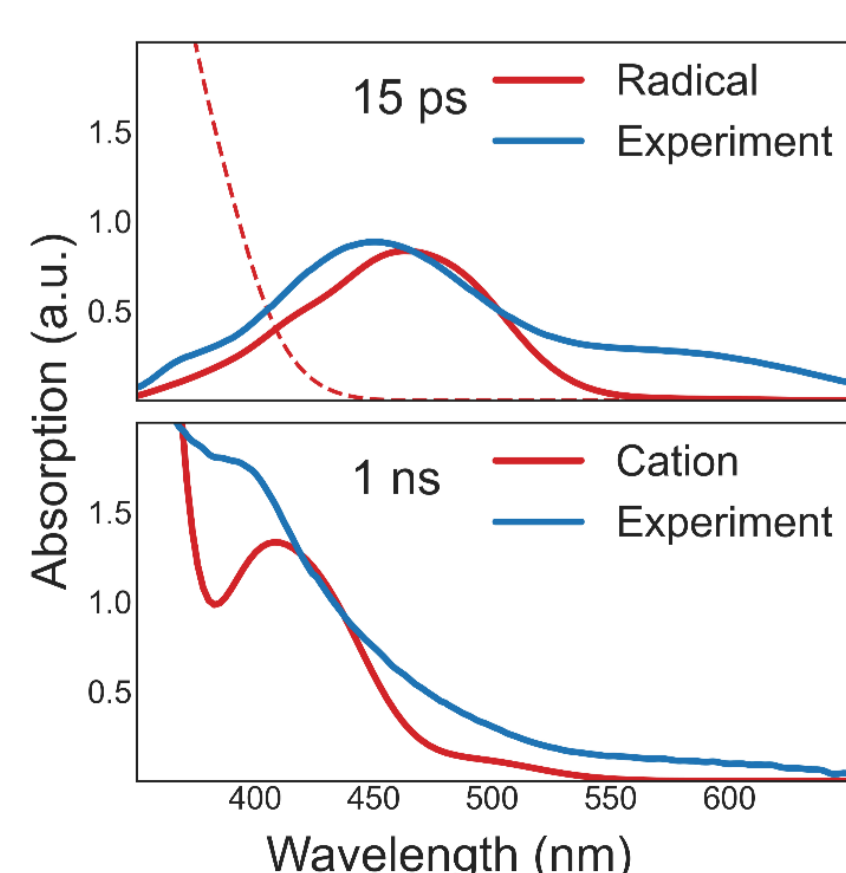
Assignments



fs timescale: $S_1(n\pi^*)$ in the Franck-Condon region

ps timescale: $T_1(\pi\pi^*)$ with Lewis acid attached

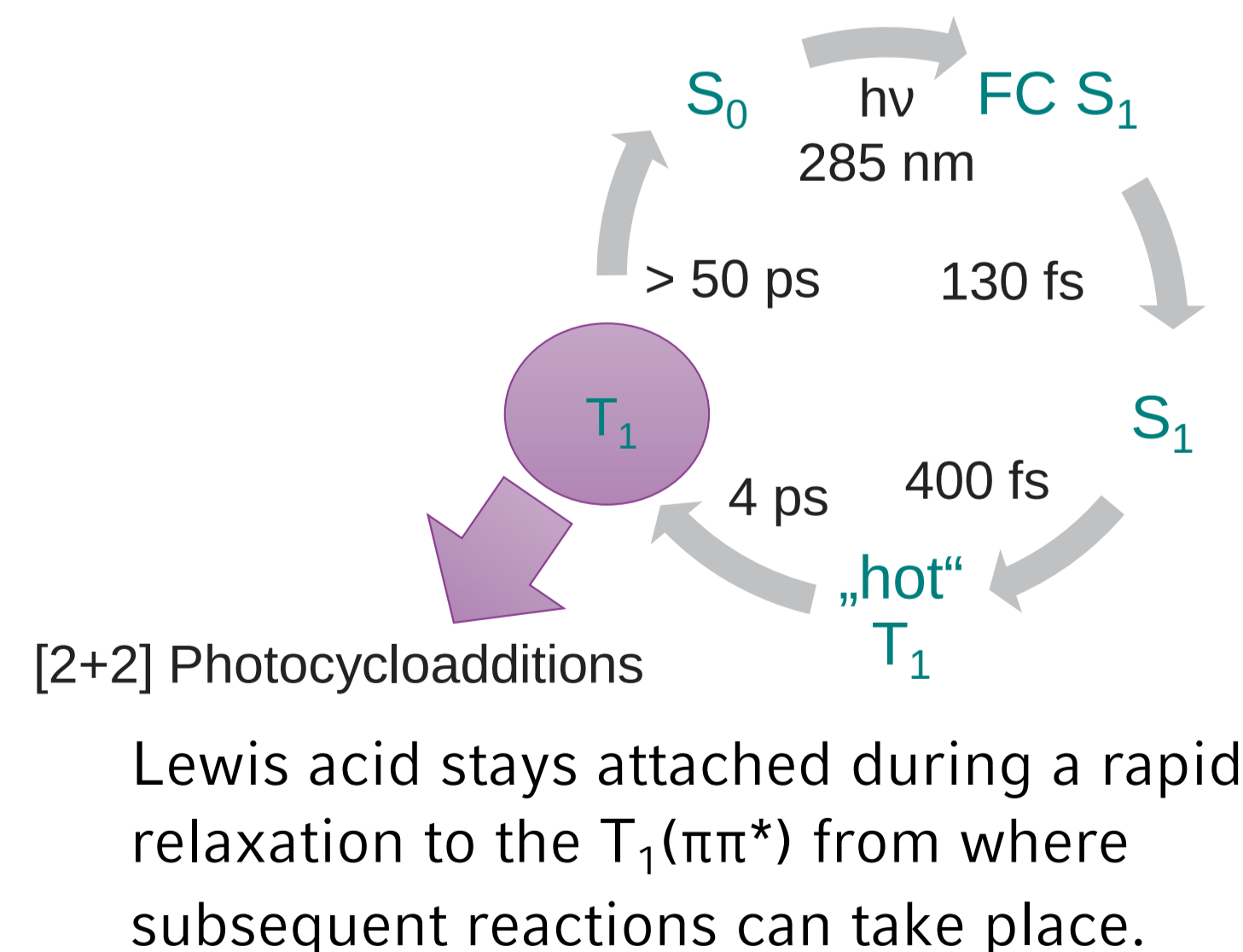
Comparison of evolution associated decay spectra with calculated excited state absorbance (XMS-CASPT2) at critical points; Spectra calculated using Wigner sampling



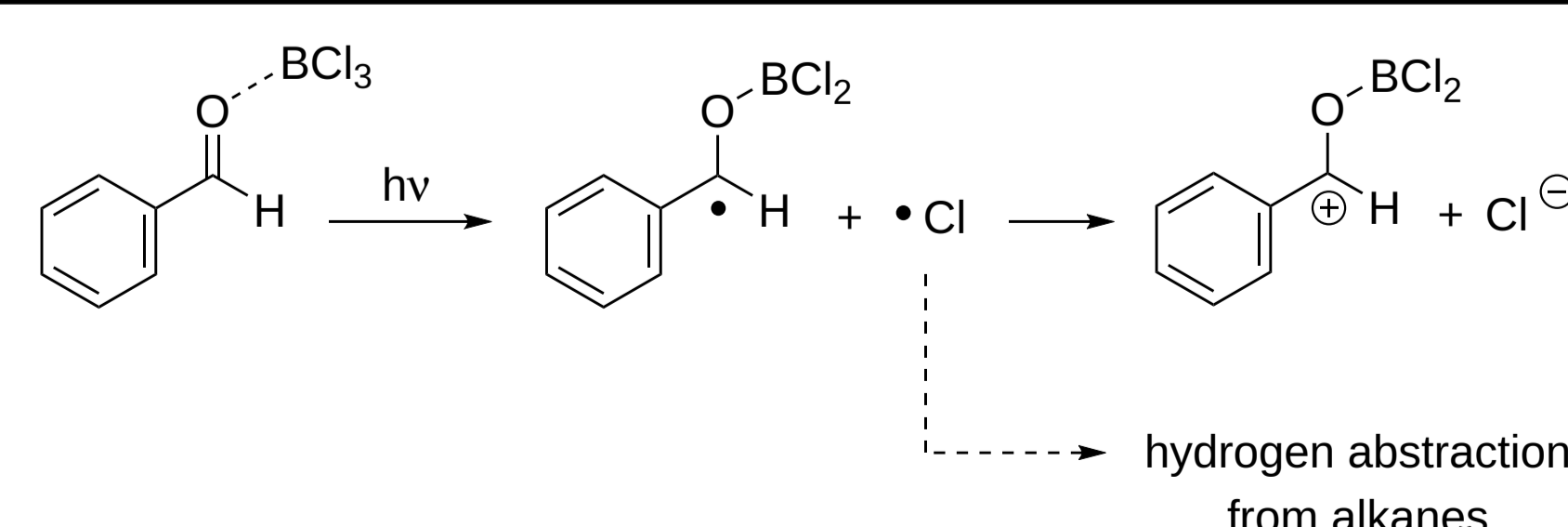
ps timescale: borylated ketyl radical

ns timescale: cation formation

Conclusions



Lewis acid stays attached during a rapid relaxation to the $T_1(\pi\pi^*)$ from where subsequent reactions can take place.



UV irradiation leads to homolytic cleavage of B-Cl bond on a femtosecond-to-picosecond timescale. Chlorine radicals can be used in subsequent reactions. In absence of a reaction partner, electron transfer is observed.

REFERENCES

- [1] E. García-Expósito et al., *J. Org. Chem.* **2001**, *66*, 26, 8811-8814.
- [2] C. Brenninger et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 14338-14349.
- [3] M. T. Peschel et al., *Angew. Chem.* **2021**, *133*, 18, 10243-10251.
- [4] A. Jain et al., *J. Chem. Theory Comput.* **2016**, *12*, 11, 5256-5258.
- [5] S. Mai et al. SHARC2.1, sharcmd.org (2019).
- [6] D. P. Schwinger et al. Manuscript submitted (2022).

