Anti-Kasha dynamics investigated with quantum-mechanically derived force-fields and non-adiabatic molecular dynamics

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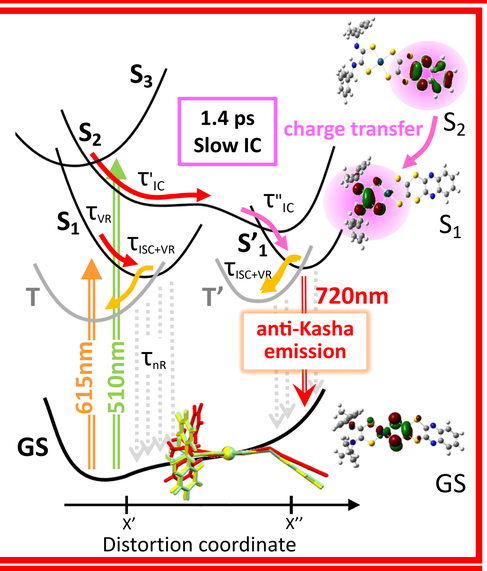
Introduction:

It was recently reported that Pt quinoxdt dithiolene complexes have a photochemical response, which markedly depends on the excitation wavelength leading to an anti-Kasha (AK) behavior. AK originates from a competition between the functional process in the upper photo-excited state and internal conversion towards the lowest excited state. Experimental evidence shows that internal conversion, which is typically a few femtoseconds, is in these systems astonishingly slowed down to 1-2 ps.[1-2]

In addition, the excitation into higher excited states seems to allow the systems to access long-lived conformational configurations not accessible from the lowest excited state. Such systems have raised considerable interest because of the possibility to conceive multi-response molecular devices or to explore novel photochemical routes.

This rich body of experimental evidence motivated us to start a computational study based on using time-dependent density functional theory aimed at clarifying the unanswered questions: low efficiency of the internal conversion, photocycle, intermediated states and structure of the long-lived configuration. Thus, fully understanding the AK behavior in these systems and in perspective optimize their performance.

In this contribution, we will explore the excited state dynamics using two complementary approaches: Surface Hopping including Arbitrary Couplings (SHARC)[3-4] and quantum derived force field Joyce[5-7]. We will also show the unique advantages of the two approaches while validating the performance of Joyce against QM data. For SHARC, we will present preliminary data.

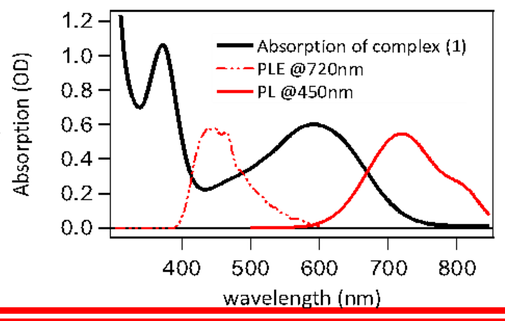


Experimental evidence: [1-2]

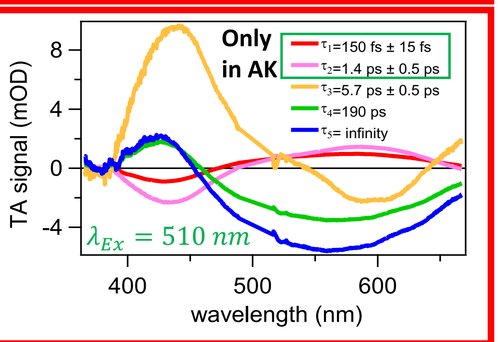
Emission @ 720 nm observed in complex (1) with maximum of PLE spectrum at 450nm instead of 600nm (the maximum of the lowest OA band)

⇒

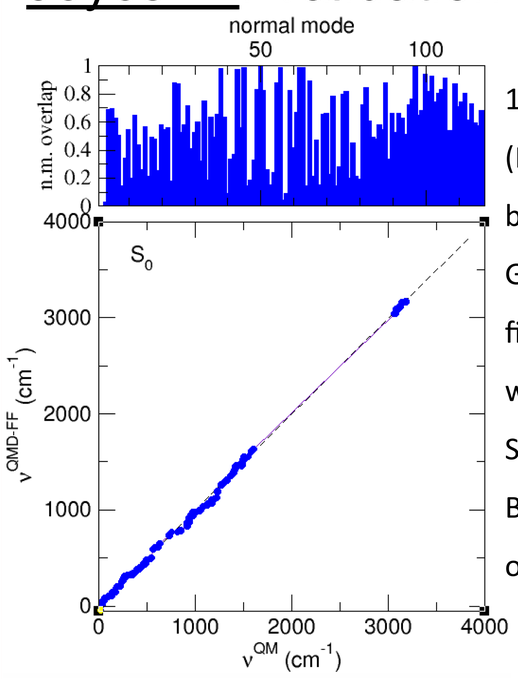
anti-Kasha emission



τ_1 and τ_2 describe a rise of the signal of the lowest excited states and are present upon AK excitation only → both describe IC from different higher excited states to the lowest one; **τ_2 corresponds to an exceptionally slow ps IC process**.

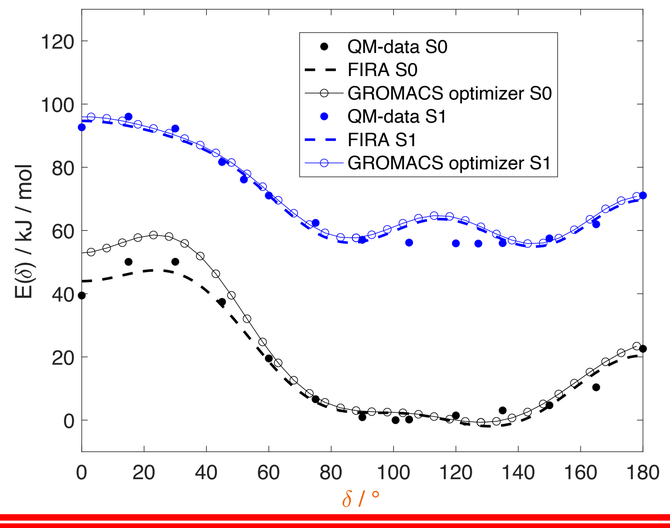


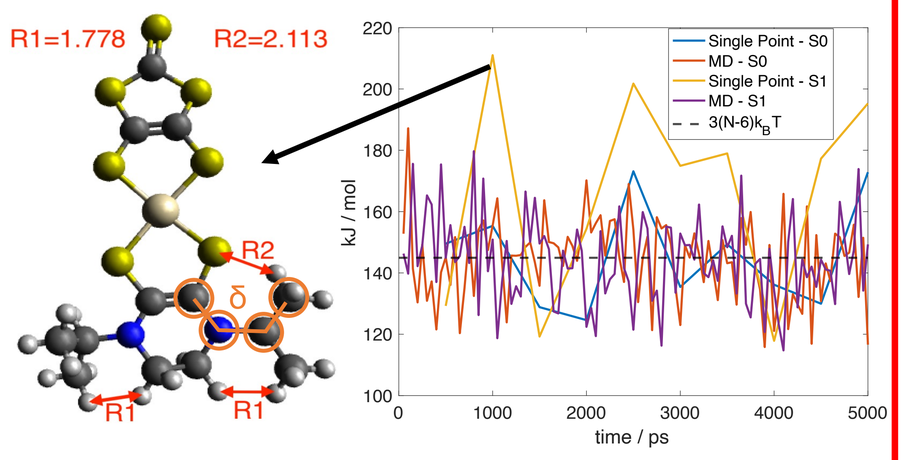
Joyce[5-7]: Validation against QM data



1) Normal mode (NM) comparison between the QM and GROMACS (topology file was produced with Joyce) for the S0. Top: overlap; Bottom: comparison of frequency values

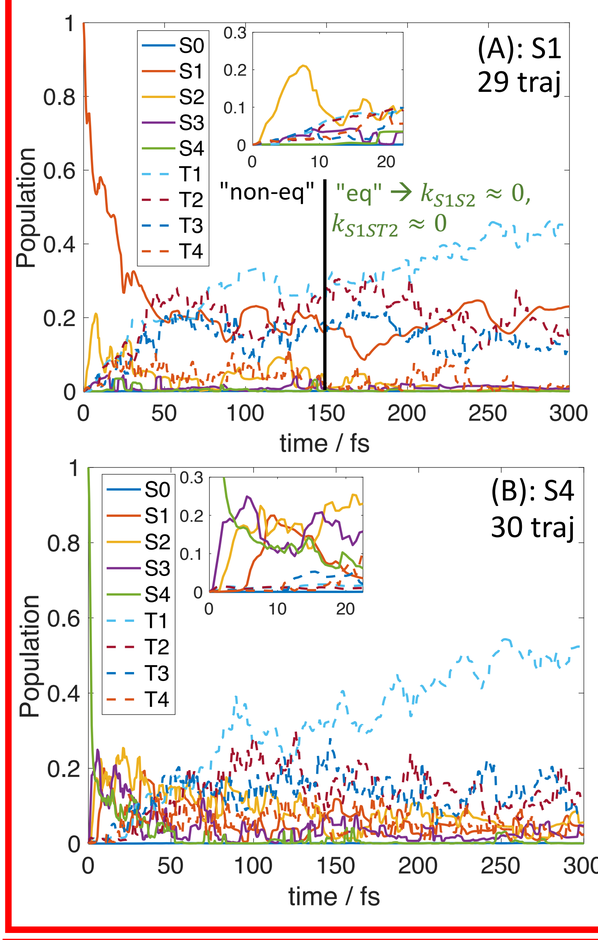
2) Comparing the potential surface energy of the flexible dihedral with two different approaches: FIRA, and GROMACS optimizer.





3) MD in vacuum: regularly extracting snaps, doing a single point (SP) calculation, comparing it with $3(N-6)\,k_bT$. SP have energies above and below the average energy. Would it compare with a regularly used force field (FF), such as OPLS-FF.

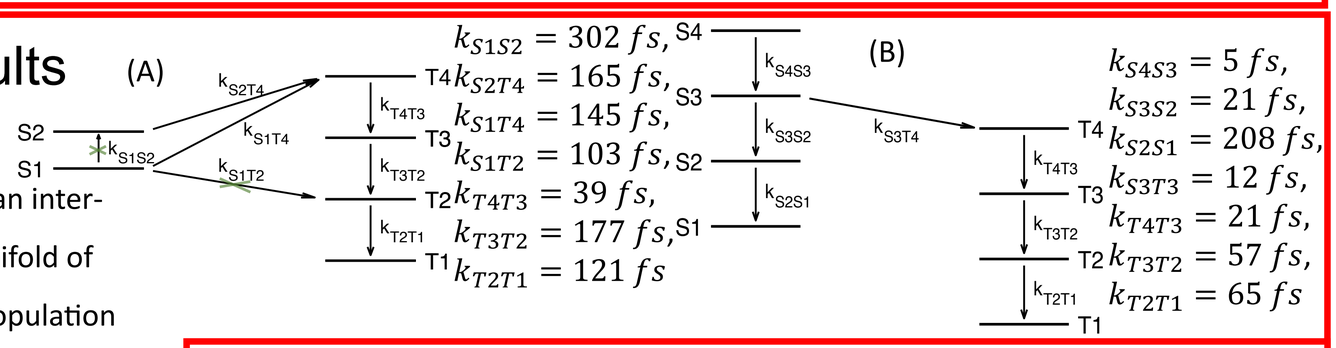
SHARC[3-4] (nonadiabatic MD): Prelimary results



(A): Upon population of S1: S2 is unexpectedly populated, followed by an inter-system crossing (ISC) towards the manifold of triplet (T) states. Remarkably the S1 population stays relatively high. T1 population rises to 50%. T2 and T3 are populated to approx. 10 % each.

(B): Upon population of S4: a sequential population from S3 to S1 is triggered and the Triplets states are similarly populated. Now S2 shows a longer population whereas S1 is short-lived.

Comparison (A) — (B): The triplet states dynamics are rather similar, despite the (B) shows a rise twice slower the final populations are comparable. We observe a marked difference in the singlet states dynamics. This could shine new light on the origin of the AK behaviour.



Further research:

Joyce: This makes it possible to extend the computable timescale. Investigations on the reaction of the solvent to the excitation are possible. To explain the solvation time measured by our group [8].

SHARC: Calculate dynamics starting from higher quinoxdt centered states (up to S10) and evaluate which orbitals are involved. In this way, we covered the most likely AK states. We started to use the linear vibronic coupling (LVC) [9] model within SHARC for rigid molecules such as the Homoleptic Pt complex [10].

Acknowledgments:

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References: [1] M. Gazzetto, F. Artizzu, S. S. Attar, L. Marchio, L. Pilia, E. J. Rohwer, T. Feurer, P. Deplano, A. Cannizzo, *The journal of physical chemistry. A* **2020**, *124*, 10687-10693. [2] S. Attar, D. Espa, F. Artizzu, L. Pilia, A. Serpe, M. Pizzotti, G. Di Carlo, L. Marchio, P. Deplano, *Inorg Chem* **2017**, *56*, 6763-6767. [3] S. Mai, P. Marquetand and L. González, WIREs Comput. Mol. Sci., 2018, e1370; [4] Mai, S.; D. Avagliano, M. Heindl, P. Marquetand, M.F.S.J. Menger, M. Oppel, F. Plasser, S. Polonius, M. Ruckenbauer, Y. Shu, D.G. Truhlar, L. Zhang, P. Zobel, L. González. *SHARC3.0: Surface Hopping Including Arbitrary Couplings: Program Package for Non-Adiabatic Dynamics*, 2023; https://sharc-md.org/. [5] Cacelli and G. Prampolini, "Parametrization and Validation of Intramolecular Force Fields Derived from DFT Calculations" J. Chem. Theory Comput., 3, 1803 (2007). [6] V. Barone, I. Cacelli, N. De Mitri, D. Licari, S. Monti and G. Prampolini "JOYCE and ULYSSES: integrated and user-friendly tools for the parameterization of intra-molecular force fields from quantum mechanical data" Phys. Chem. Chem. Phys., 15, 3736 (2013). [7] Cerezo, J., Prampolini, G. and Cacelli, I. Developing accurate intramolecular force fields for conjugated systems through explicit coupling terms. Theoretical Chemistry Accounts, 137, 80 (2018). [8] F. Frei, A. Rondi, D. Espa, M. L. Mercuri, L. Pilia, A. Serpe, A. Odeh, F. Van Mourik, M. Chergui, T. Feurer, P. Deplano, A. Vlček Jr. and A. Cannizzo, Dalton Trans., 2014, 43, 17666. [9] F. Plasser, S. Gómez, M. F. S. J. Menger, S. Mai and L. González, *Phys. Chem. Chem. Phys.*, 2019,**21**, 57-69. [10] S. Attar D. Espa, F. Artizzu, M. L. Mercuri, A. Serpe, E. Sessini, G. Concas, F. Congiu, L. Marchiò and P. Deplano, *Inorg. Chem.* 2016, 55, 11, 5118–5126.