Non-adiabatic MD analysis for TURBOMOLE

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1 Introduction

The theoretical formalism used to compute observables from the trajectory data of non-adiabatic molecular dynamics (NAMD) simulations is outlined in this document. The particular example used here is that of a dually fluorescent molecule 4-(Dimethylamino)benzonitrile (DMABN) in the gas phase, where emission occurs from a locally excited (LE) state and a charge transfer (CT) excited state.

2 Computational Details

Twenty NAMD trajectories were propagated for 1.5 ps starting from the bright S_2 state, with initial conditions sampled from a 10 ps long ground-state molecular dynamics trajectory. Electronic structure calculations were performed using density functional theory (DFT) with the ωB97X-D [1] functional and the def2-SVP basis set [5] for all atoms. Excited state properties were computed using time-dependent density functional theory (TDDFT). All calculations were performed with the TURBOMOLE program suite, Version V7.5 [2]

State	**Excitation energy (eV)**	**f**
S_1 (L_b)	4.76	0.03
S_2 (L_a)	5.03	0.55

Table 1: Vertical excitation energies (eV) and oscillator strengths in the length gauge of DMABN computed at the TDDFT/ωB97X-D level of theory at the ground state minimum energy geometry with the experimental band origins in parenthesis

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3 Population analysis

The population of the electronically excited state k at time t, was computed as $p_k(t) = \frac{N_k(t)}{N_{\text{traj}}}$, where $N_k(t)$ is the number of trajectories that are evolving on the state k at time t and N_{traj} is the total number of trajectories.

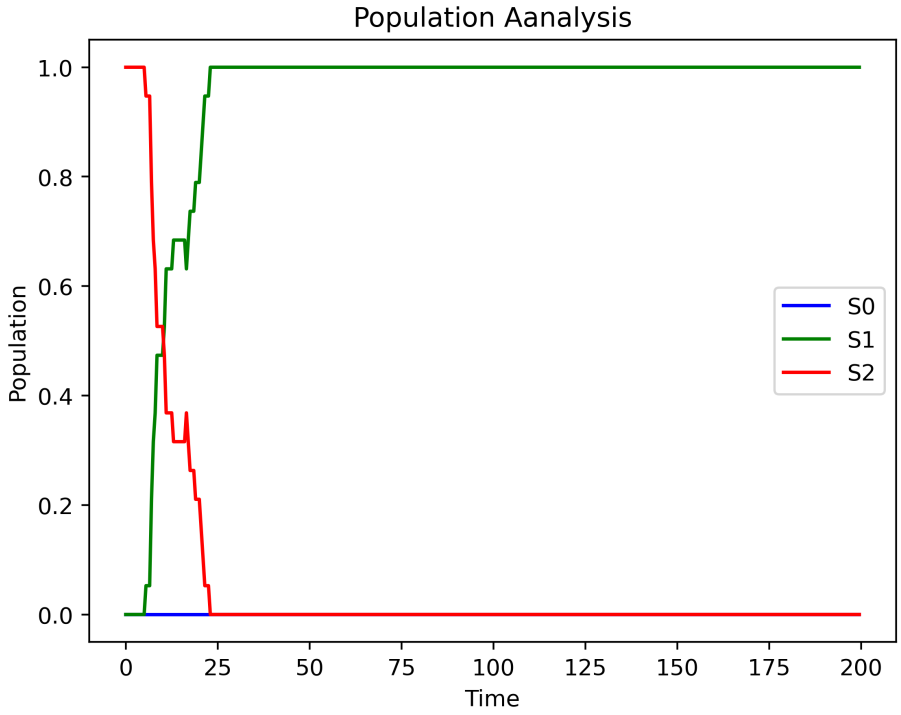

Figure 1: Population analysis of the swarm of NAMD trajectories of DMABN after initial excitation to the S_2 state.

4 Steady state fluorescence spectrum

Spectroscopic observables are obtained by ensemble averaging over the set of trajectories after an equilibration period of 0.5 ps. The steady-state fluorescence spectrum is constructed from the NAMD simulations using the following lineshape function [4],

$$\sigma_{em}(\omega) = \frac{1}{N} \sum_{j=1}^{N} f_{j,a} \omega_{j,a}^2 \, G(\omega_{j,a} - \omega) \tag{1}$$

where $f_{j,a}$ is the oscillator strength of the active state a of the trajectory, ω is the excitation energy, N is the total number of time steps from the trajectories after the equilibration period and G is a Gaussian or Lorentzian broadening function.

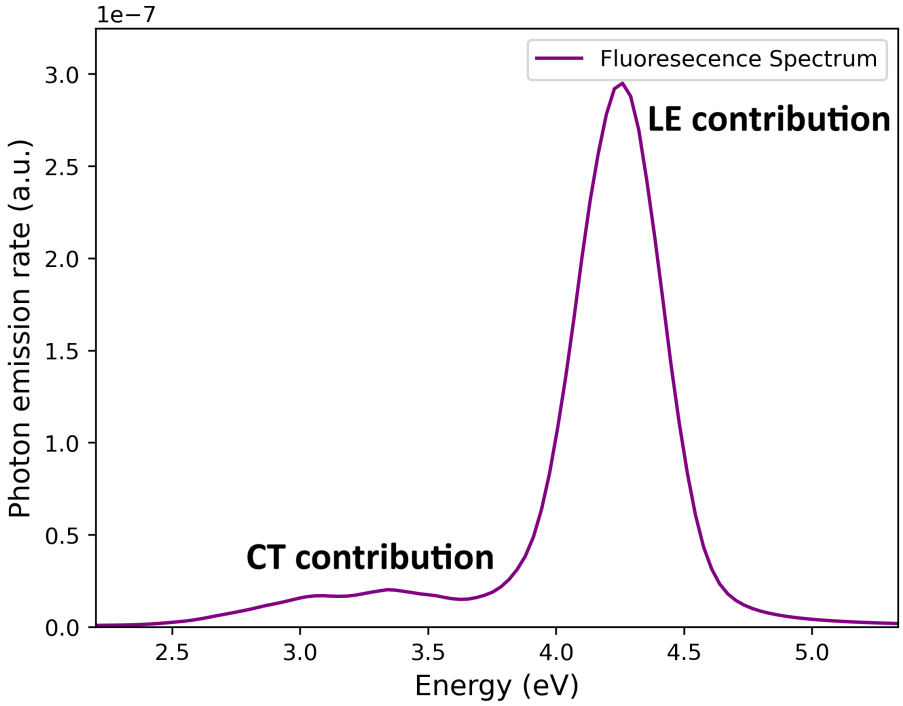

Figure 2: The steady state Fluorescence spectrum of DMABN computed from the NAMD trajectories exhibiting emission from the locally excited (LE) state and the charge transfer (CT) state.

5 Time resolved fluorescence spectrum

The time-resolved fluorescence spectrum is computed using the following lineshape function [3],

$$I^{TRF}(\omega, t) = \frac{1}{N_{traj}} \sum_{j=1}^{N_{traj}} f_{j,a}(t)\omega_{j,a}(t)^2 G(\omega_{j,a} - \omega) \tag{2}$$

Work in Progress!!!

References

[1] Jeng-Da Chai and Martin Head-Gordon. "Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections". In: *Physical Chemistry Chemical Physics* 10.44 (2008), pp. 6615–6620.

[2] Yannick J Franzke et al. "TURBOMOLE: Today and tomorrow". In: *Journal of chemical theory and computation* 19.20 (2023), pp. 6859–6890.

[3] Michał Andrzej Kochman and Bo Durbeej. “Simulating the nonadiabatic relaxation dynamics of 4-(N, N-dimethylamino) benzonitrile (DMABN) in polar solution”. In: *The Journal of Physical Chemistry A* 124.11 (2020), pp. 2193–2206.

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[5] Florian Weigend and Reinhart Ahlrichs. “Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy”. In: *Physical Chemistry Chemical Physics* 7.18 (2005), pp. 3297–3305.