

Excimer formation dynamics in the isolated tetracene dimer: Supplementary Material

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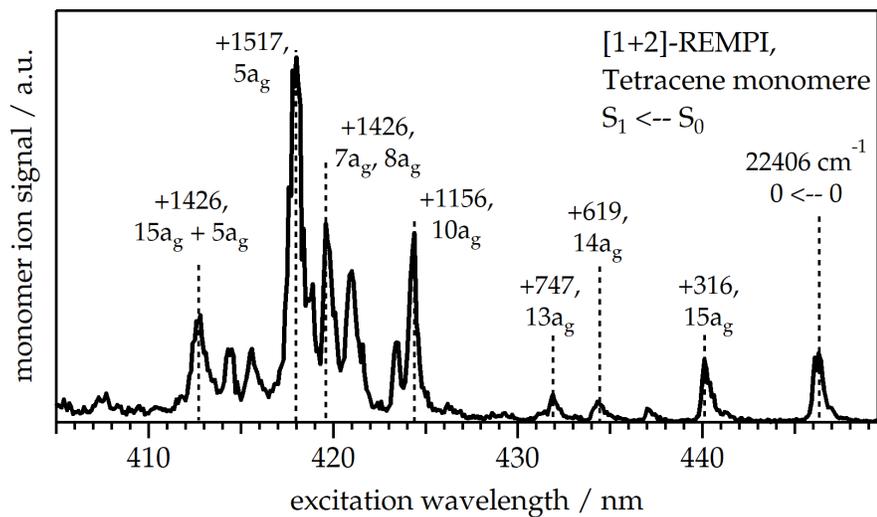


Fig. S1: The one-color REMPI spectrum of the $S_1 \leftarrow S_0$ transition of tetracene, recorded with the ps-laser system. Apart from the lower resolution due to the bandwidth of the ps-laser, the spectrum agrees well with earlier laser-induced fluorescence spectra recorded with ns-lasers.¹

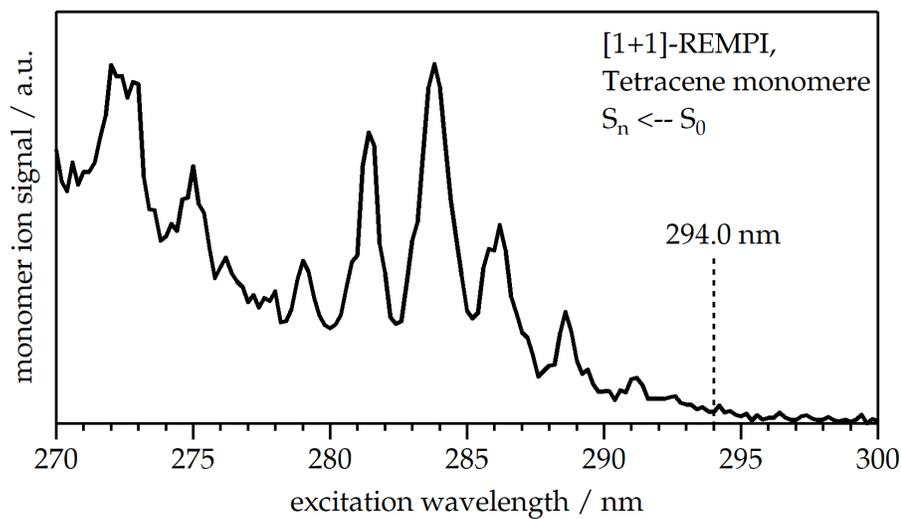


Fig. S2: The one-color REMPI spectrum of the $S_n \leftarrow S_0$ transition of tetracene. The transition has been observed before in the gas phase.² Computations indicate that it cannot be assigned to a transition into the S_2 state, but rather to a higher excited singlet state³

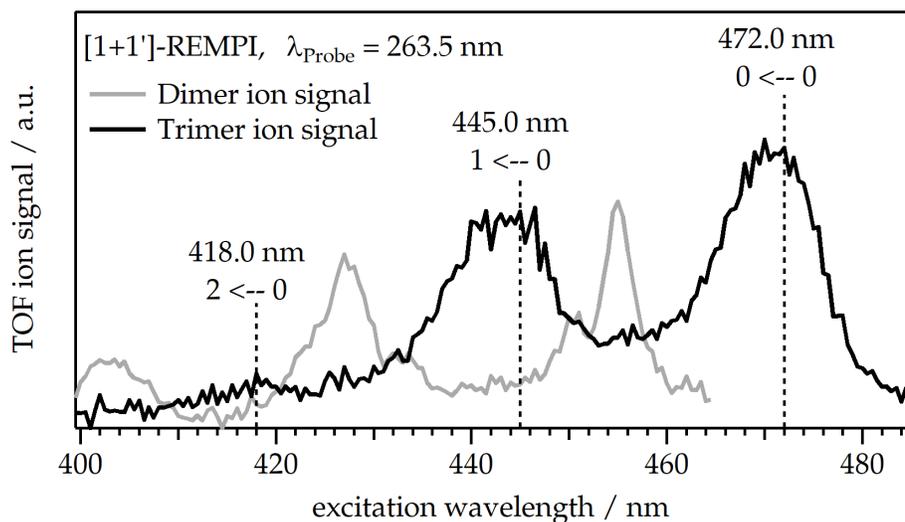


Fig. S3: In addition to the tetracene dimer (grey line), the molecular trimer has also been observed (black line). As visible, the bands are shifted with respect to each other, thus preferential excitation of dimer and trimer is possible with ps-pulses. The bands are most likely due to excited vibrations in the cluster.

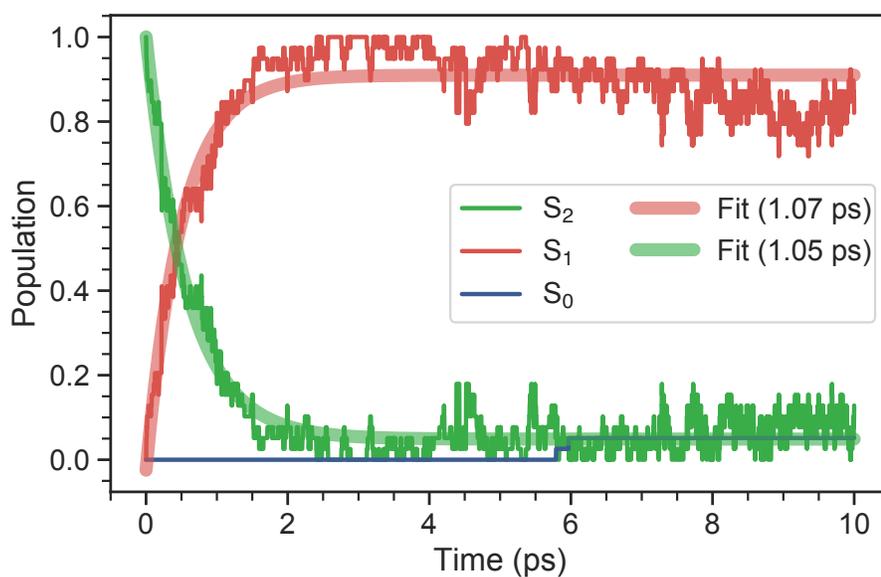


Fig. S4: Electronic state populations as a function of time at the level of TD-LC-DFTB (48e,48o).

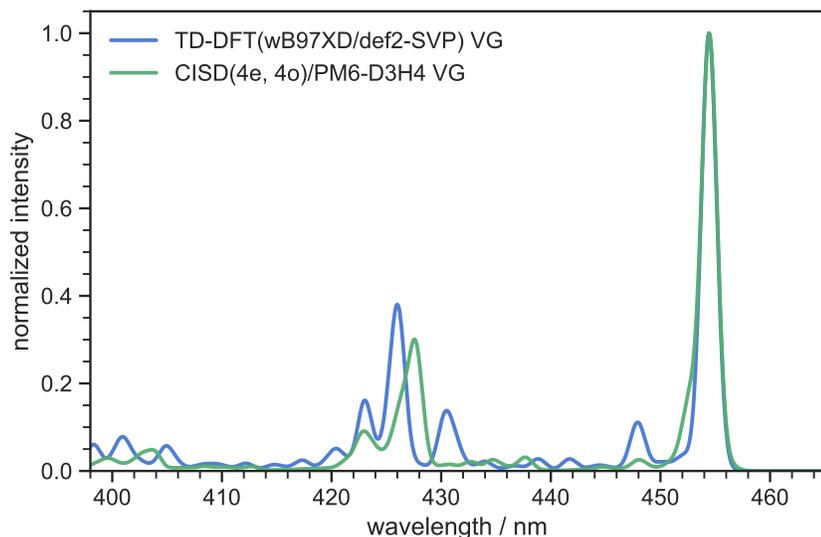


Fig. S5: Simulated vibrationally resolved absorption spectra of the most stable isomer at the TD-DFT and CISD(4e,4o) level. The TD-DFT (CISD) spectrum was shifted by 0.11 (0.92) eV for a better comparison to the experimental REMPI spectrum (Fig. 4). It should be noted that there is an energetic shift between the AH and the VG model, as only the AH model correctly accounts for the differences in the zero-point energies.

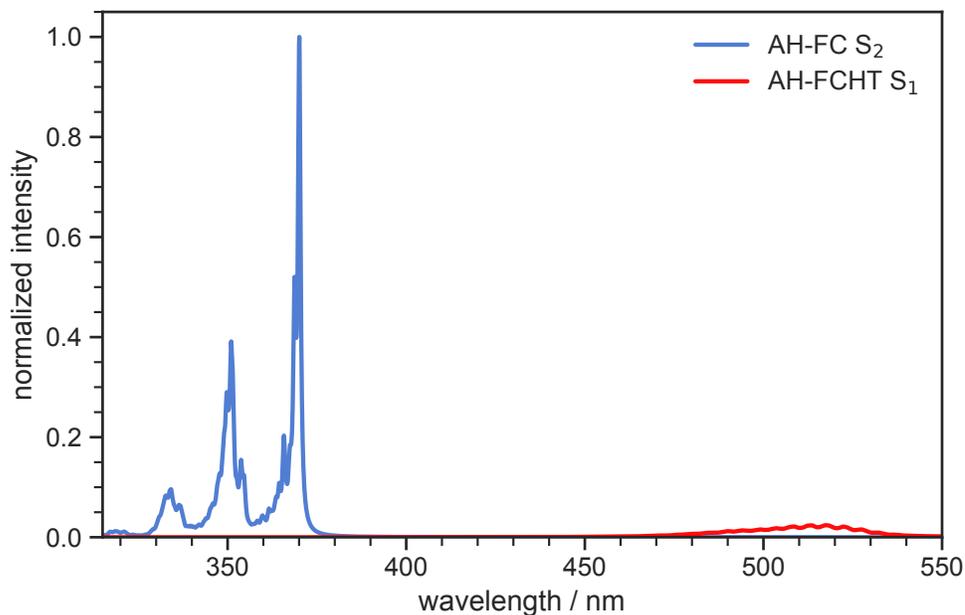


Fig. S6: Simulated vibrationally resolved absorption spectrum of the S_1 and S_2 at the TD-DFT(wB97XD/def2-SVP) level. The spectra were not shifted, to match experimental REMPI spectra. It should be noted, that the minimum of S_1 is significantly shifted compared to the ground state geometry. Therefore, it is questionable if the harmonic approximation is still valid for this transition.

References

- 1 A. Amirav, U. Even and J. Jortner, *J. Chem. Phys.*, 1981, **75**, 3770–3793.
- 2 G. C. Morris, *J. Mol. Spectrosc.*, 1965, **18**, 42–50.
- 3 S. Knippenberg, J. H. Starcke, M. Wormit and A. Dreuw, *Mol. Phys.*, 2010, **108**, 2801–2813.