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The Mechanism of Excimer Formation: An Experimental and Theoretical Study on the Pyrene Dimer: Supplementary Material

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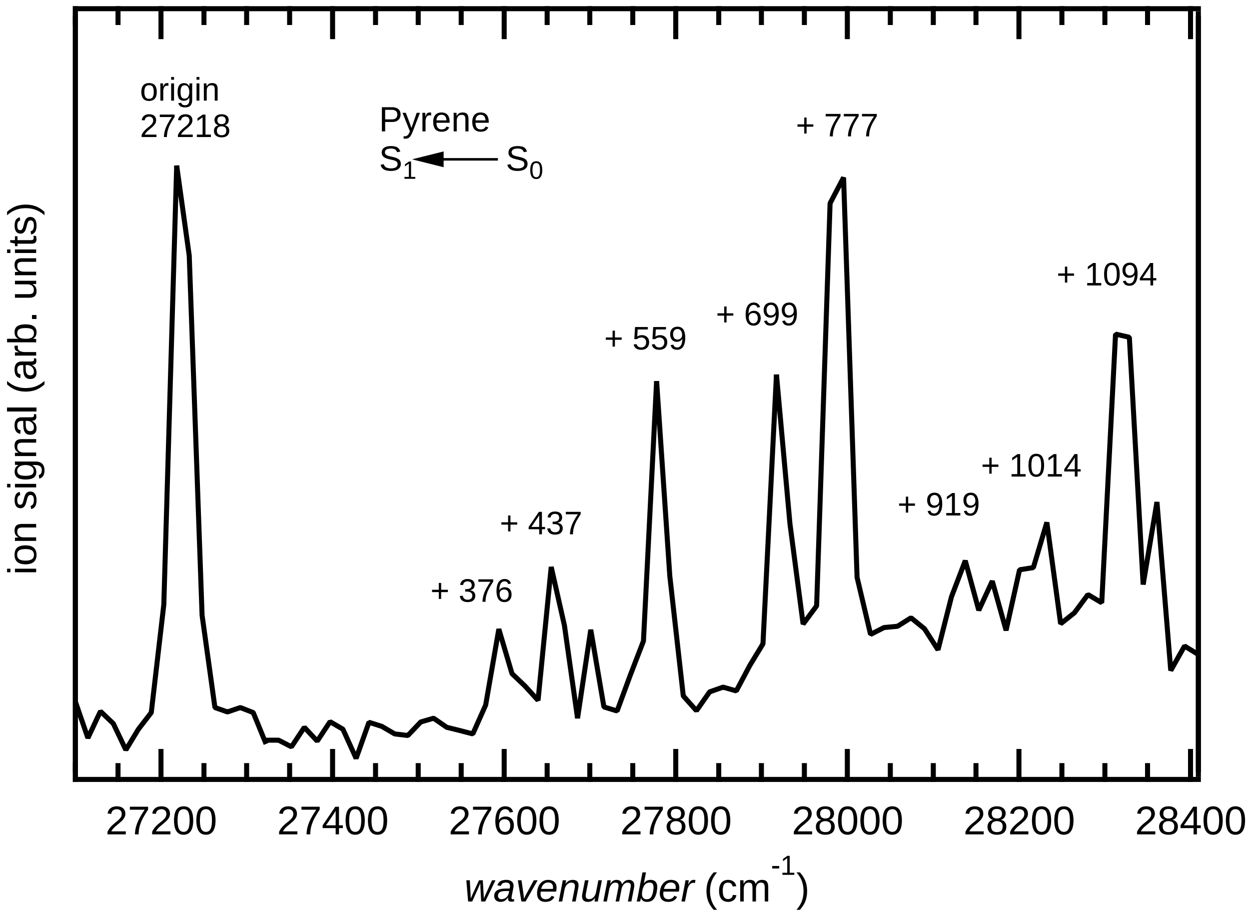

Fig. S1: $[1 + 2']$ -REMPI of the S_1 state of pyrene using 527 nm as the probe pulses. The origin was found to be 27218 cm^{-1}. Several well-resolved vibronic transitions are visible which indicate sufficient cooling in the molecular beam.

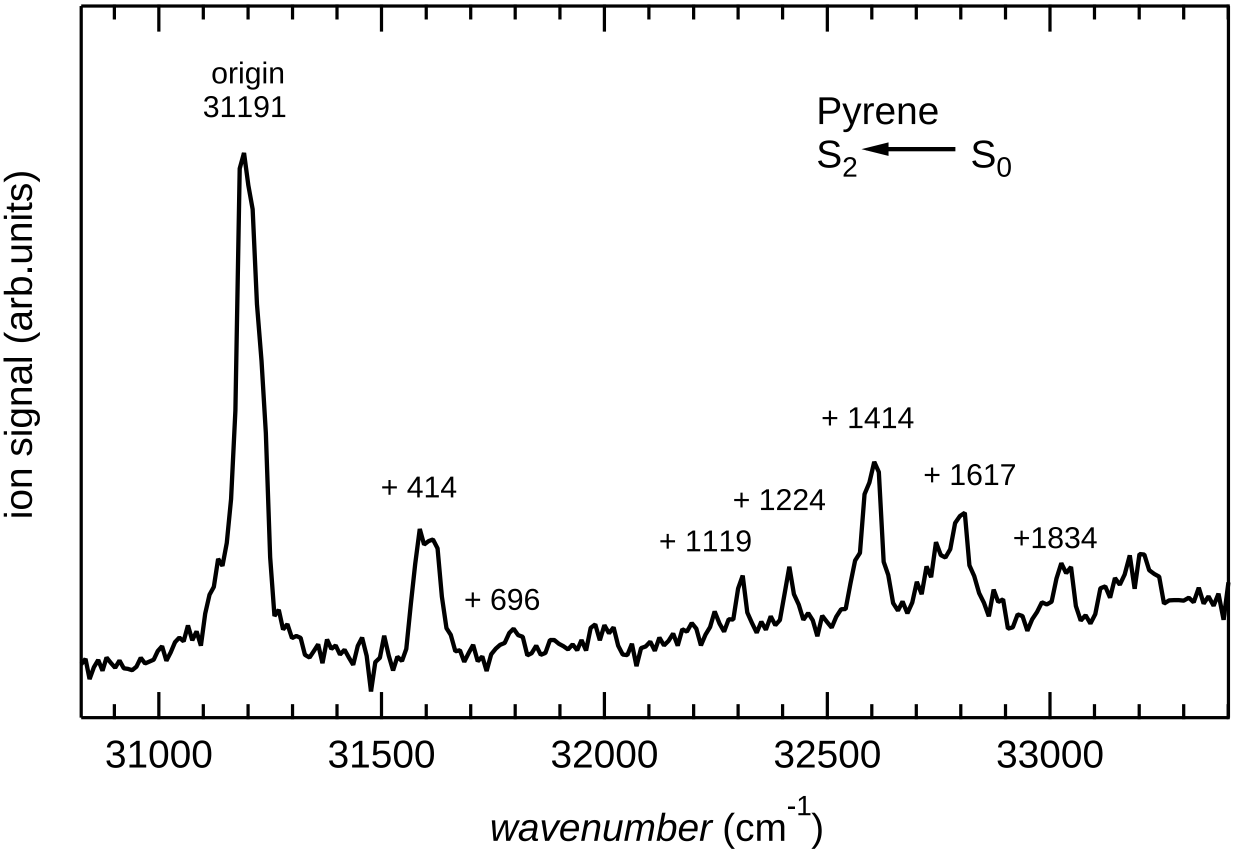

Fig. S2: $[1+2']$ -REMPI of the S_2 state of pyrene using 351 nm as the probe pulses. The origin was found to be 31191 cm^{-1}. Again several vibronic transitions are visible.

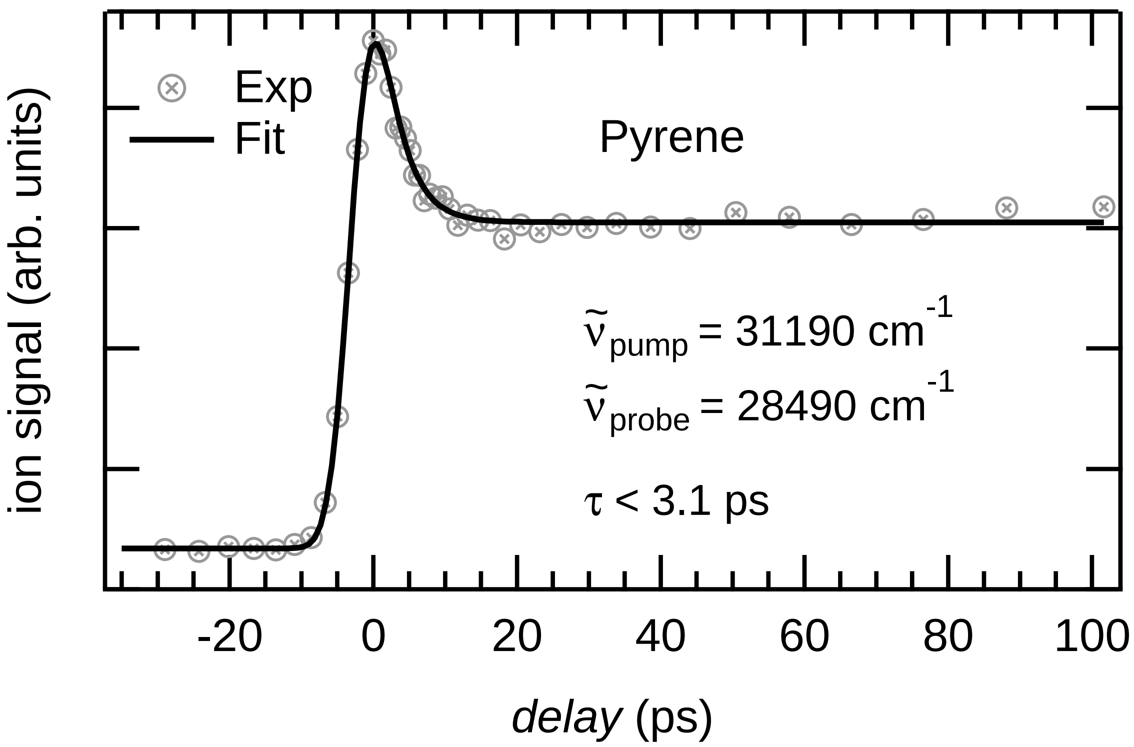

Fig. S3: Delay scan of the pyrene Monomer obtained at the origin (320.6 nm) of the S_2 state using 351 nm as the probe pulses. The signal decays rapidly (<3.1 ps) to a constant level due to IVR from the S_2 zero order state to the coupled S_1 levels.

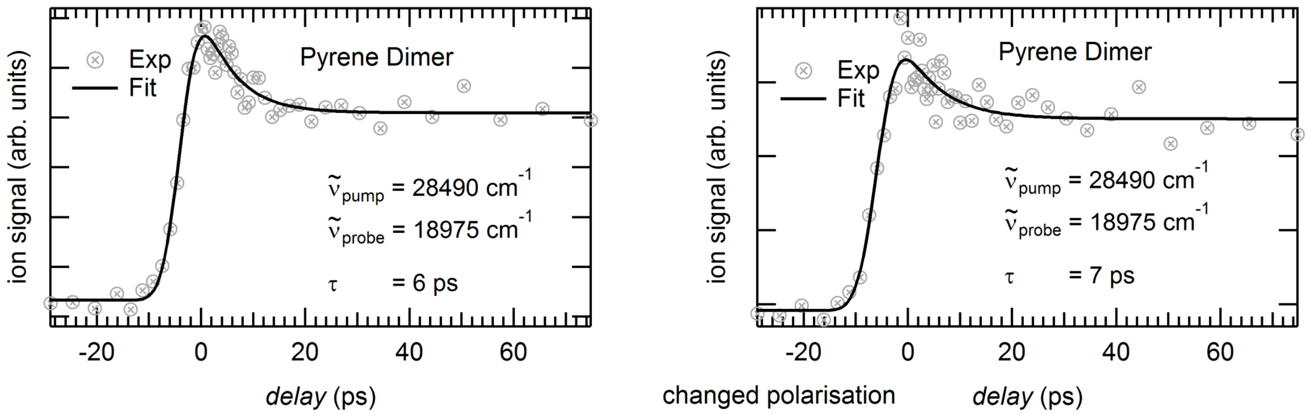

Fig. S4: Delay scans of the pyrene Dimer obtained at 351 nm excitation. The two spectra recorded with parallel (left) and perpendicular (right) polarization of pump- and probe(527 nm)-laser show very similar lifetimes. This indicates that the observed transient is not related to molecular rotation.

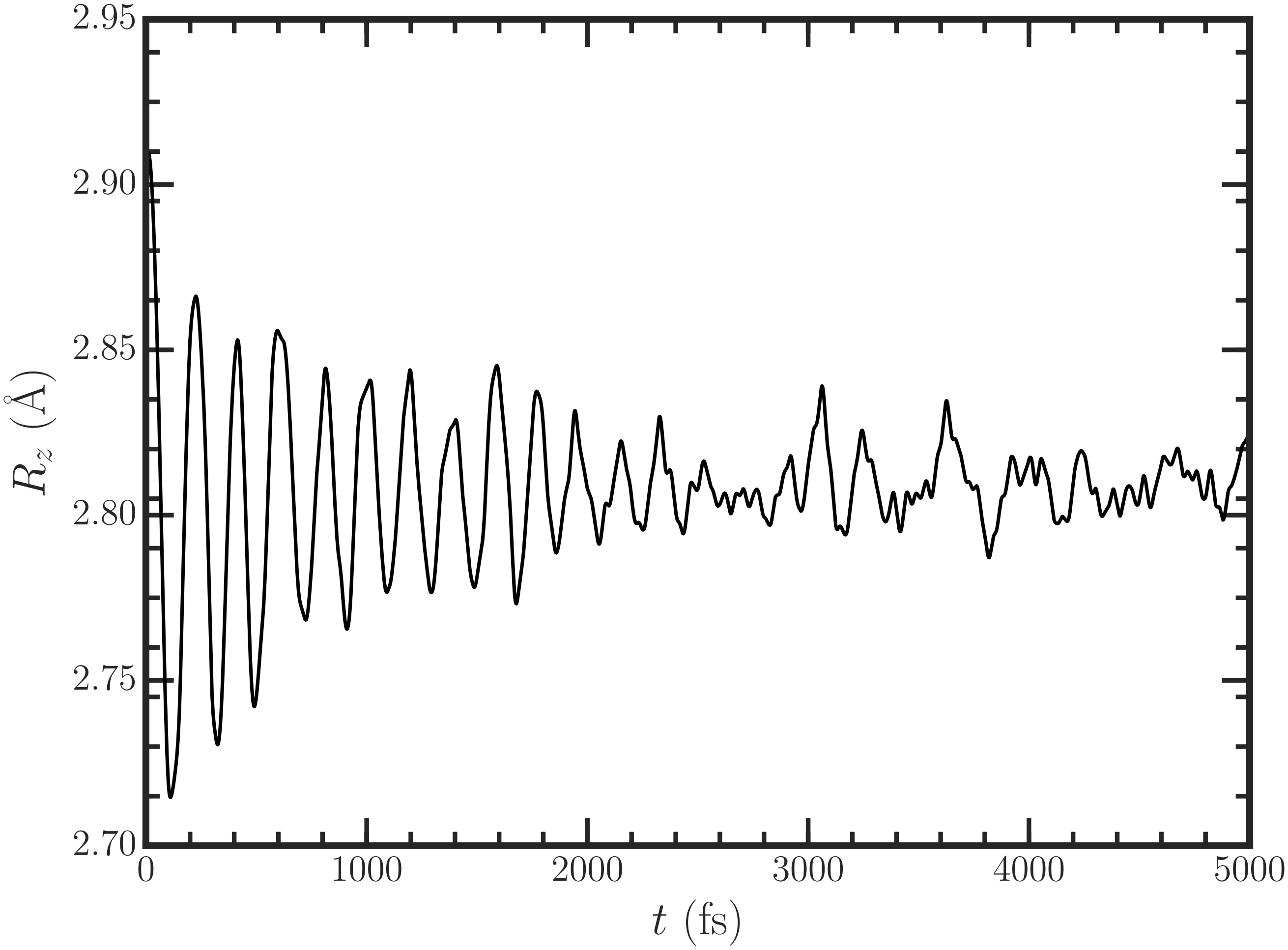

Fig. S5: Stacking distance between the pyrene monomers as a function of time averaged over an ensemble of surface hopping trajectories.

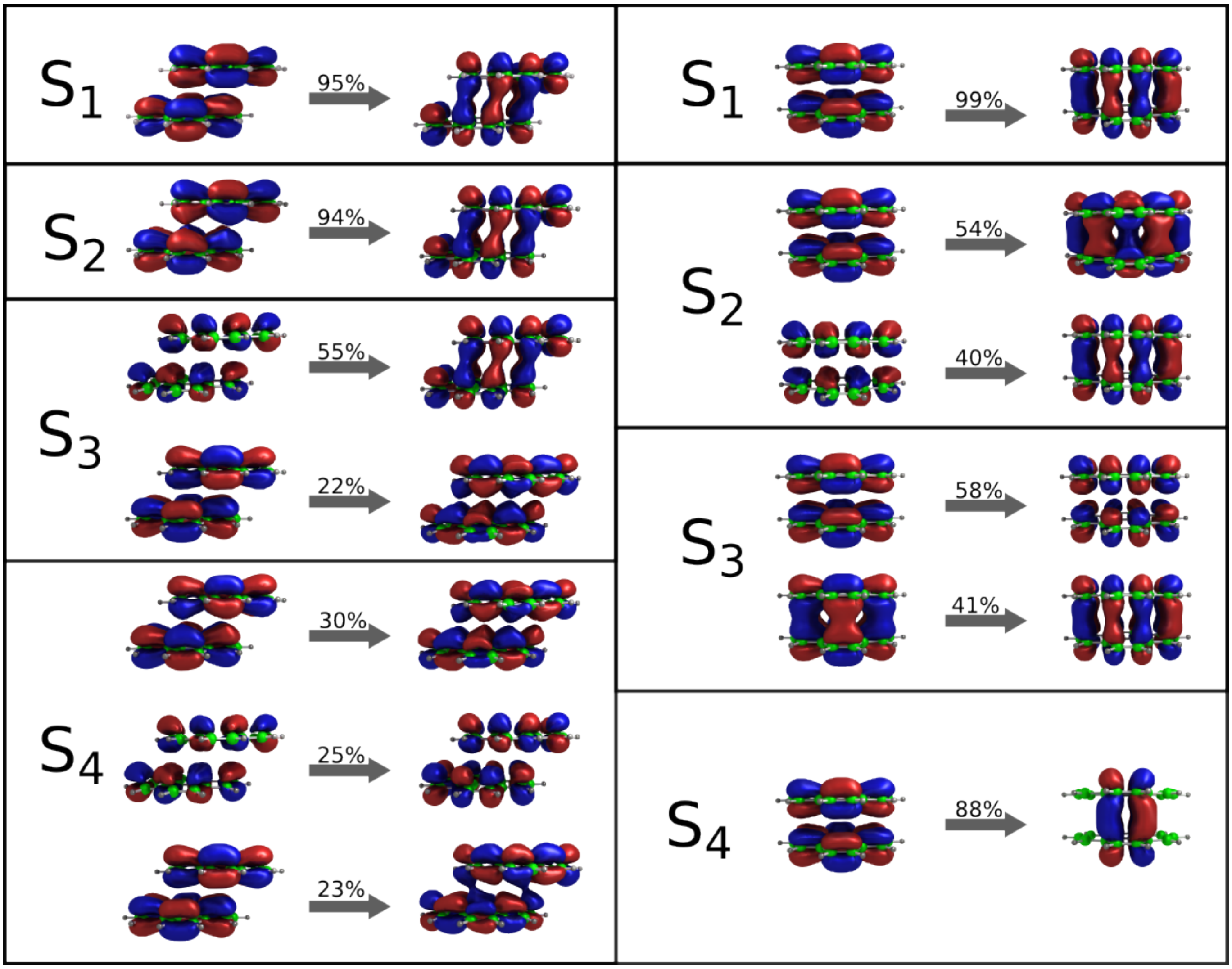

Fig. S6: Natural transition orbitals of the parallel shifted ground state geometry (left) and the fully stacked excimer structrure (right) in the framework of TDDFT CAM-B3LYP/def-2SVP.

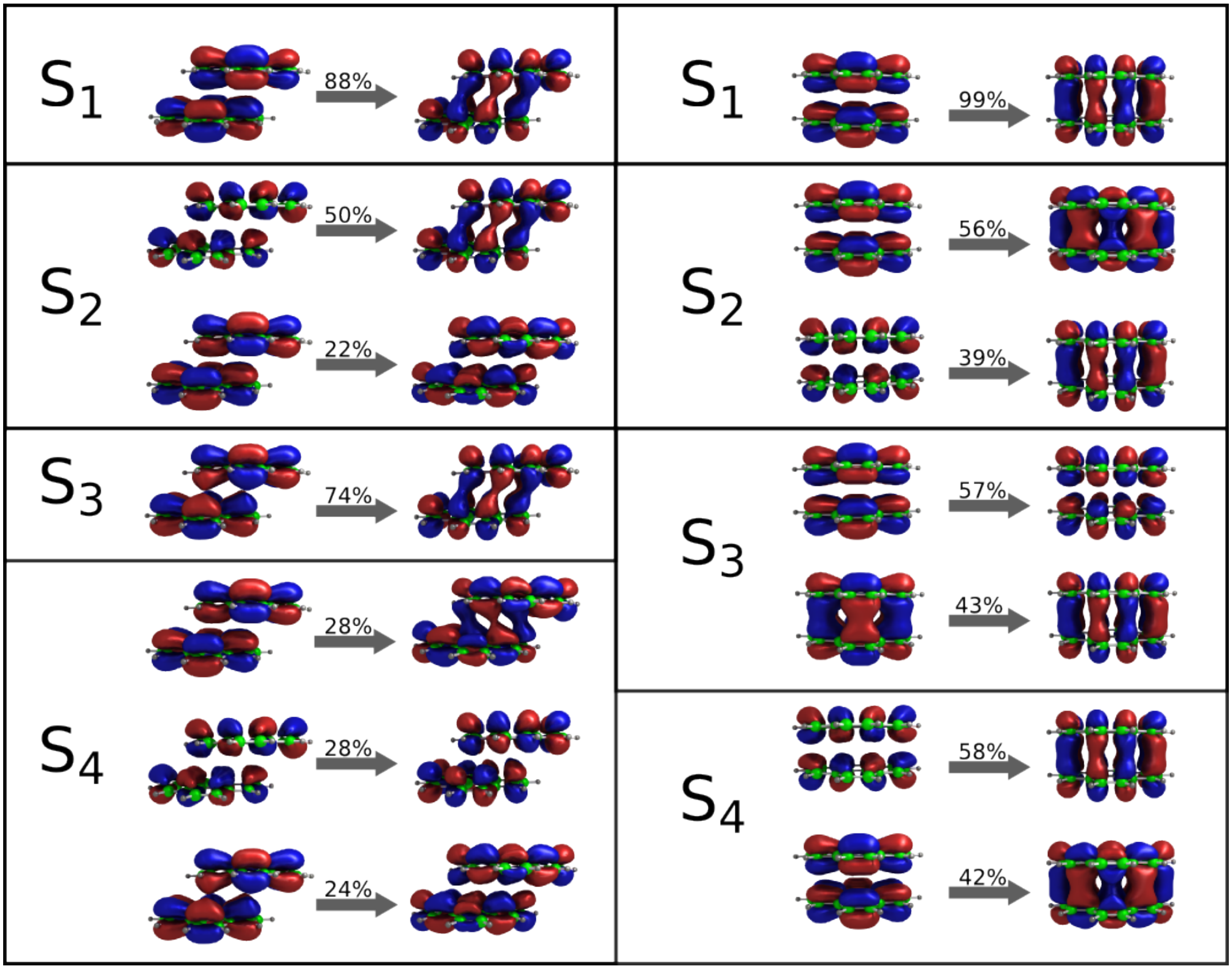

Fig. S7: Natural transition orbitals of the parallel shifted ground state geometry (left) and the fully stacked excimer structrure (right) in the framework of TDDFT BHLYP/def2-SVP.

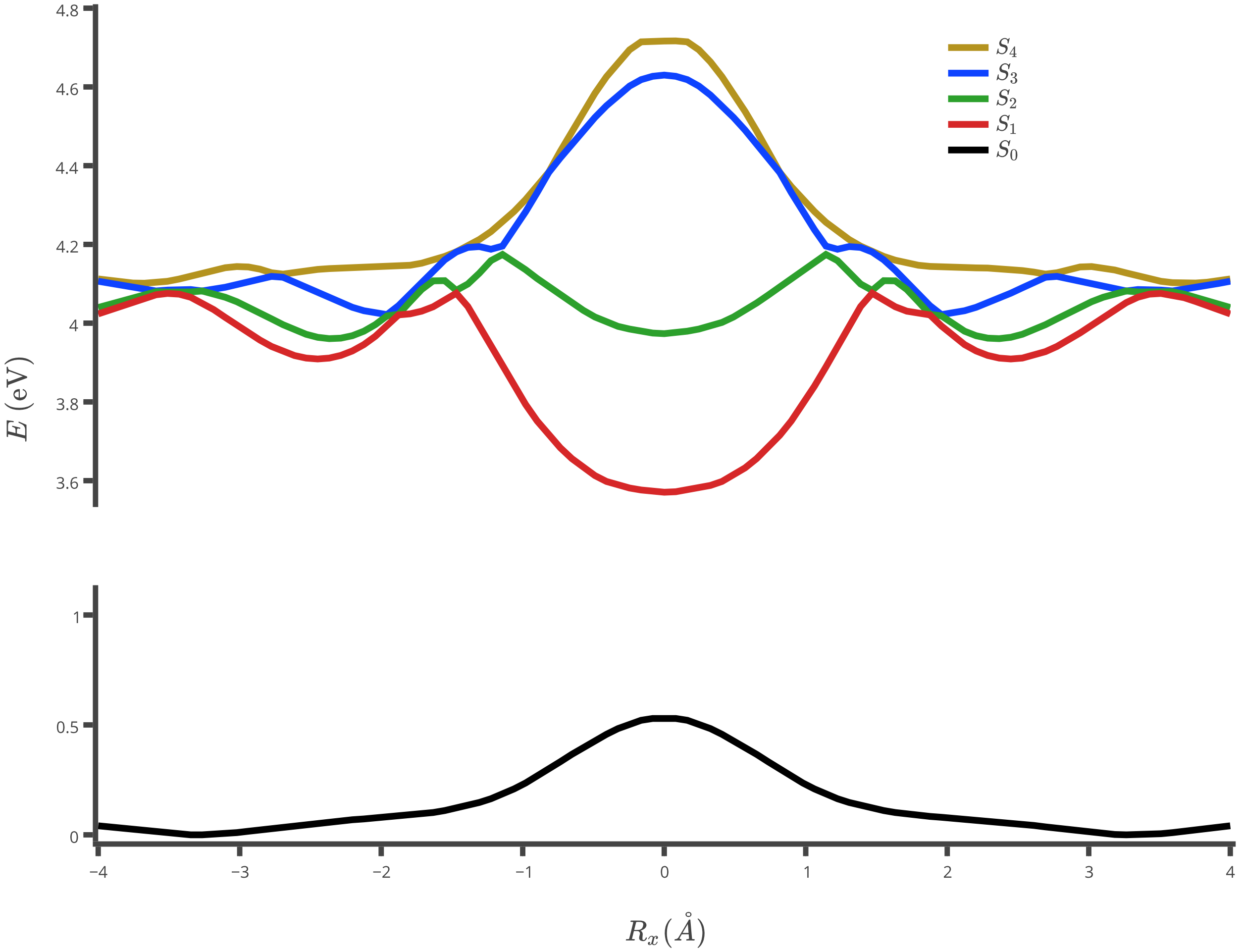

Fig. S8: Energies of the ground (S_0) and the four lowest ($S_1 - S_4$) excited states of the pyrene dimer along the parallel shift coordinate (R_x) at an interplanar distance (R_z) of 3.3 Å. (CAM-B3LYP/def2-SVP)

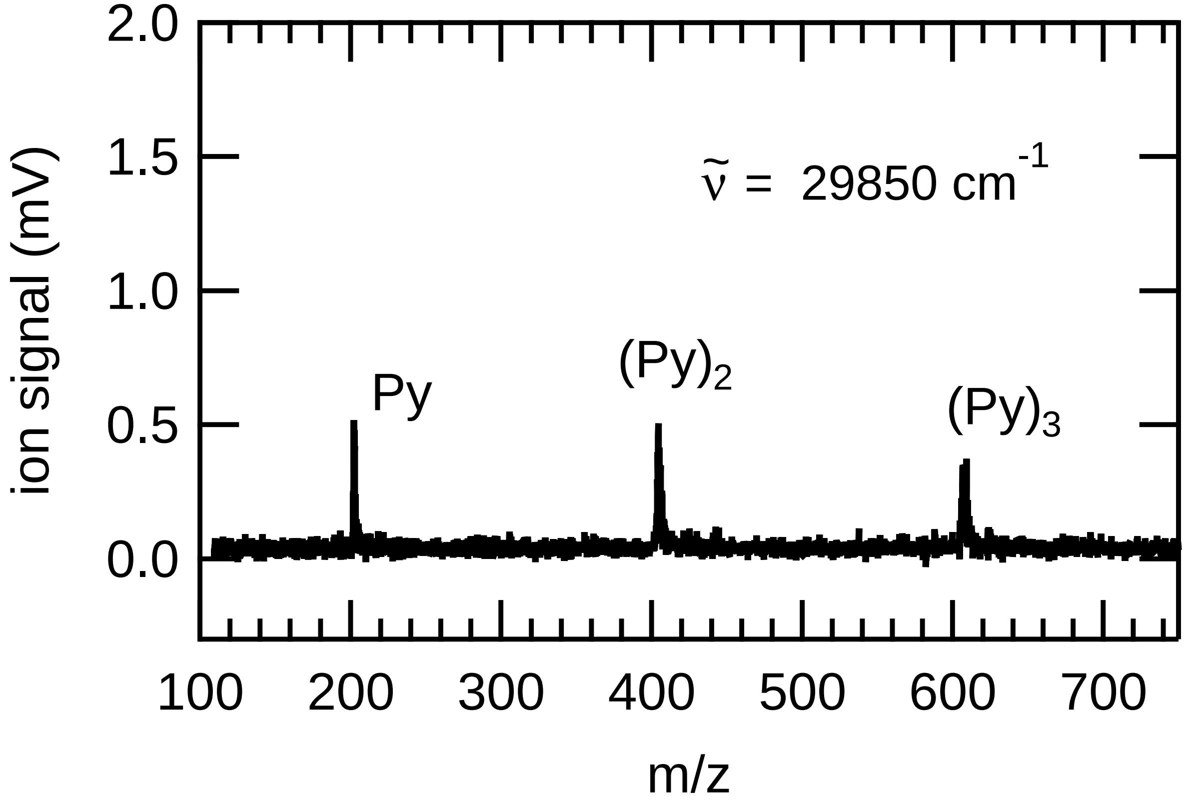

Fig. S9: Mass spectra measured at 335 nm, which corresponds to band maximum of the dimer absorption.

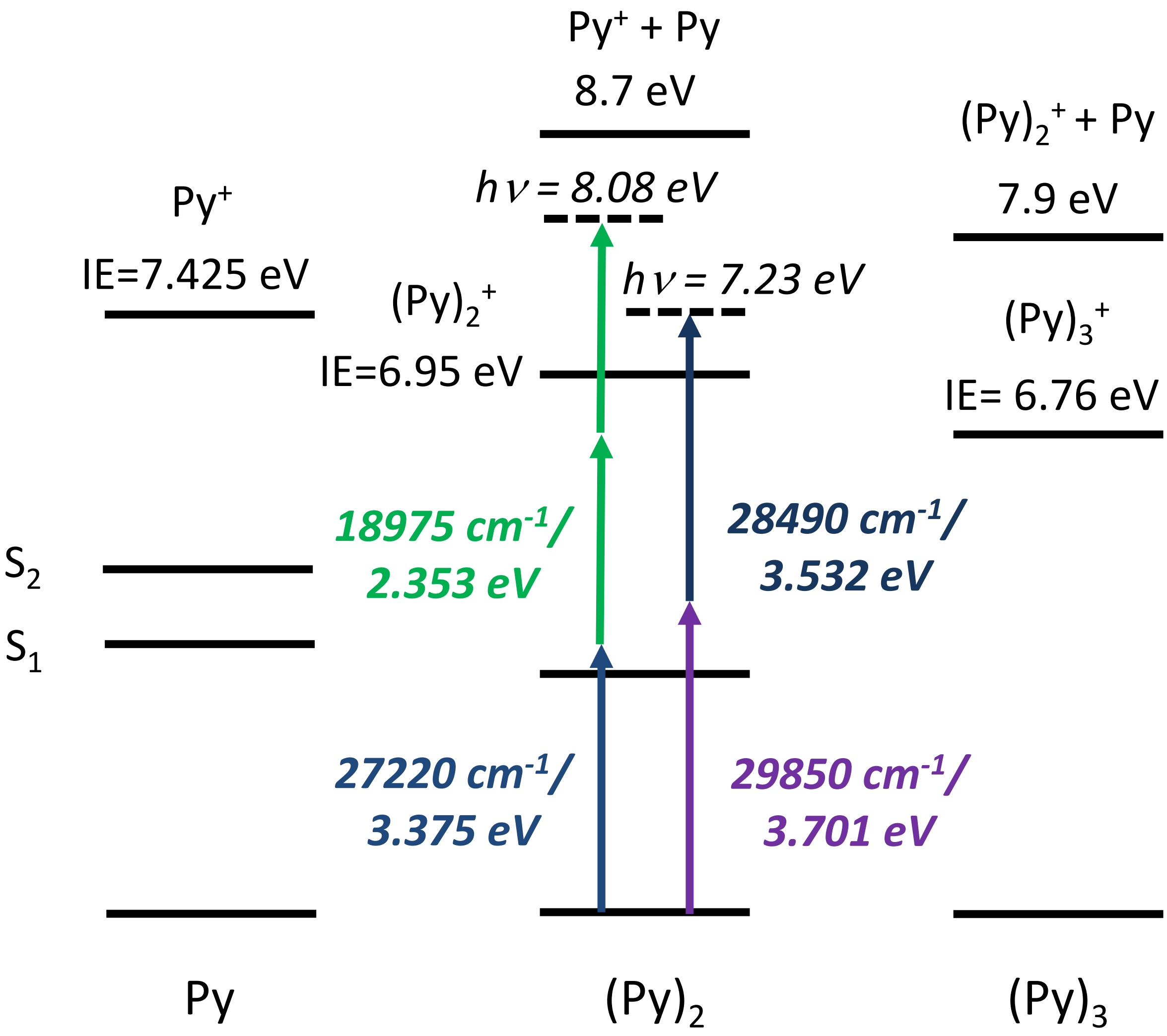

Fig. S10: Ionization and fragmentation thresholds of the pyrene monomer, dimer and trimer.

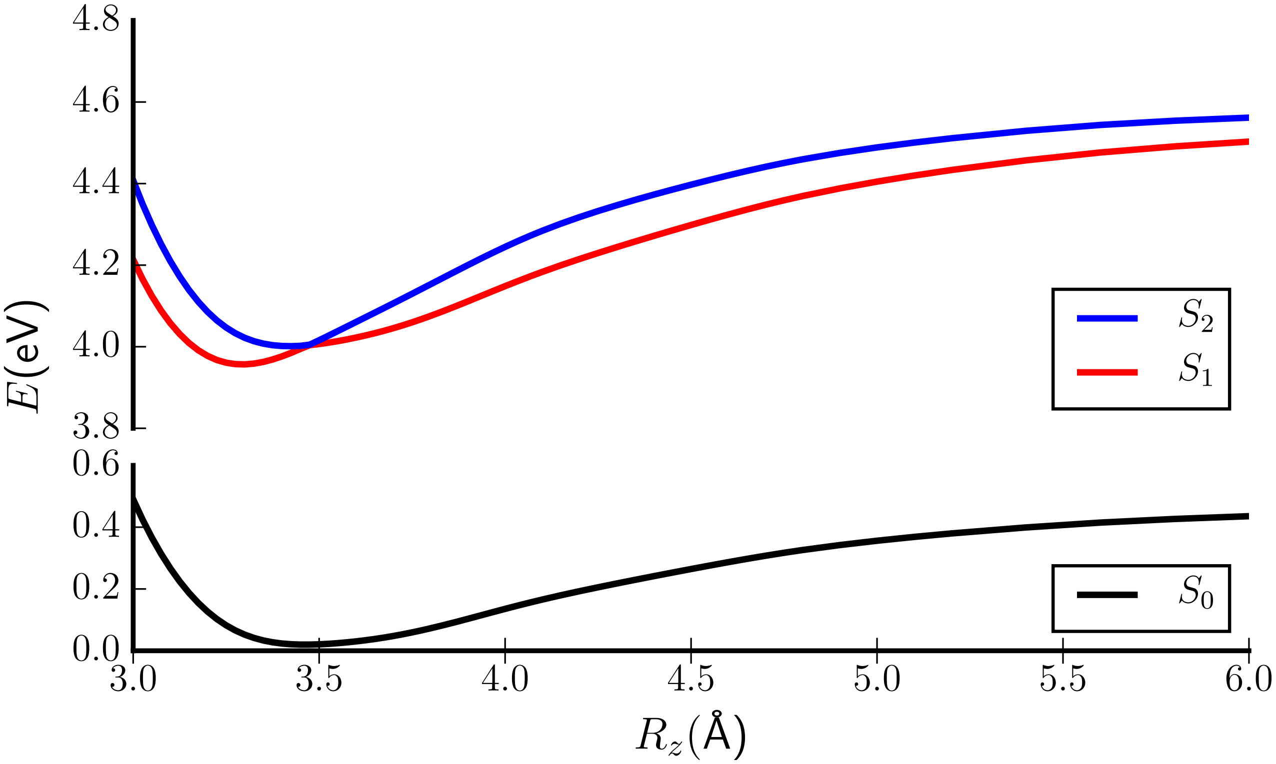

Fig. S11: Energies of the ground (S_0) and the two lowest (S_1,S_2) excited states of the pyrene dimer along the interplanar distance (R_z) in the frame of TDDFT (BH-LYP/TZVP).

Table S1: Calculated vertical transition energies of the ground state minimum of the pyrene dimer and monomer.

	Dimer S_1 (eV)	Dimer S_2 (eV)	Monomer AE (eV)
TDDFT BH-LYP [a]			
def2-SVP	3.95	3.98	4.09
6-31G*	4.01	4.04	4.14
TZVP	3.99	3.99	4.10
TDDFT CAM-B3LYP [a]			
def2-SVP	3.51	3.73	4.07
TZVP	3.57	3.82	4.08
TDDFTB[a]	3.50	3.59	3.53
MCQDPT [b]			
6-31G(d)			3.66

[a] present work

[b] Reference 66.