

Supporting Information for

Time-resolved photoelectron spectroscopy of 4-(dimethylamino)benzethyne - An experimental and computational study

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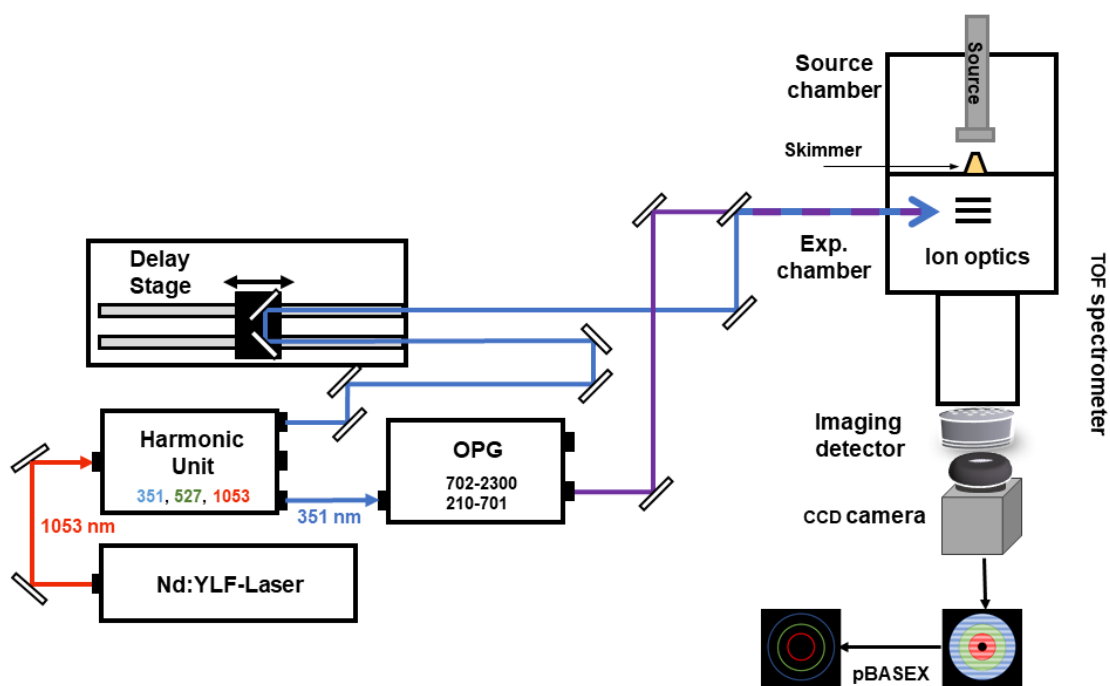


Fig. S1: Schematic depiction of the experimental setup of the picosecond time-resolved experiments at the Julius-Maximilians-Universität Würzburg.

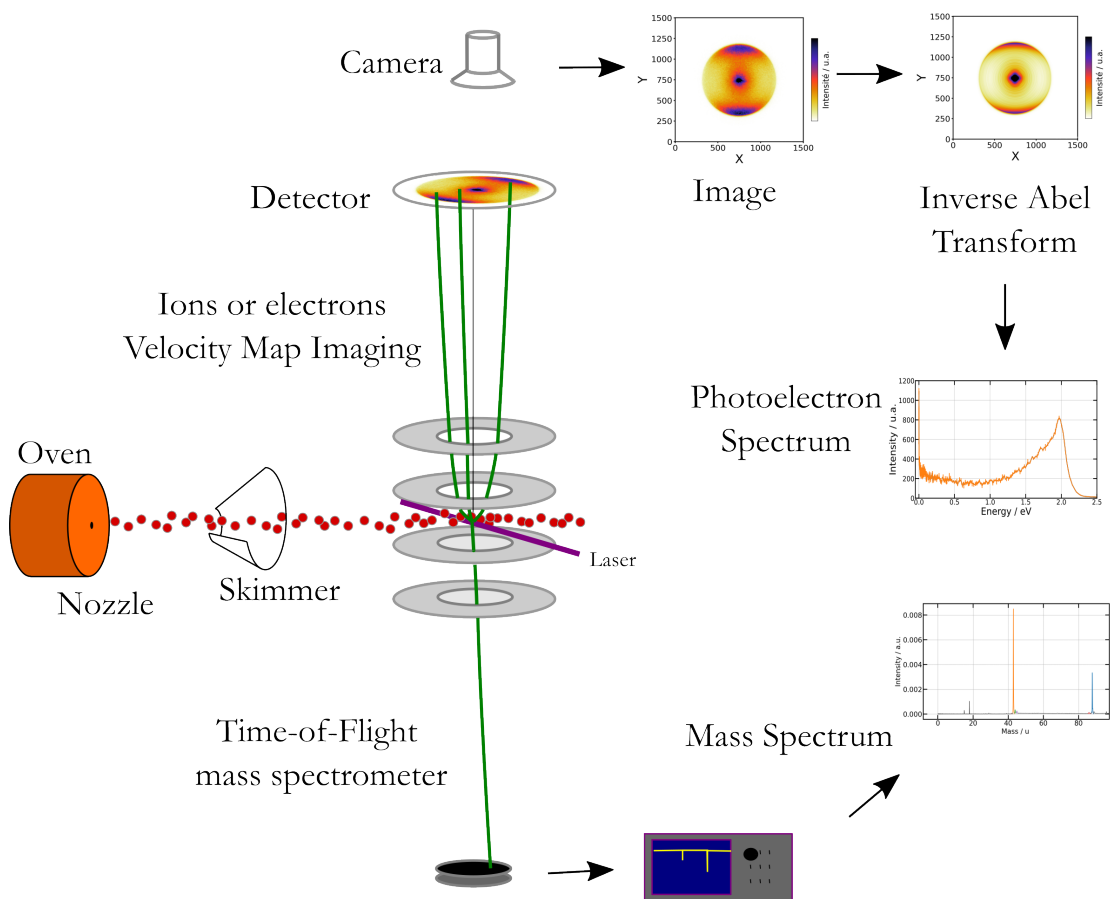


Fig. S2: Schematic depiction of the experimental setup of the femtosecond time-resolved experiments that was used at the ATTOLab laser platform at LIDYL, Université Paris-Saclay.

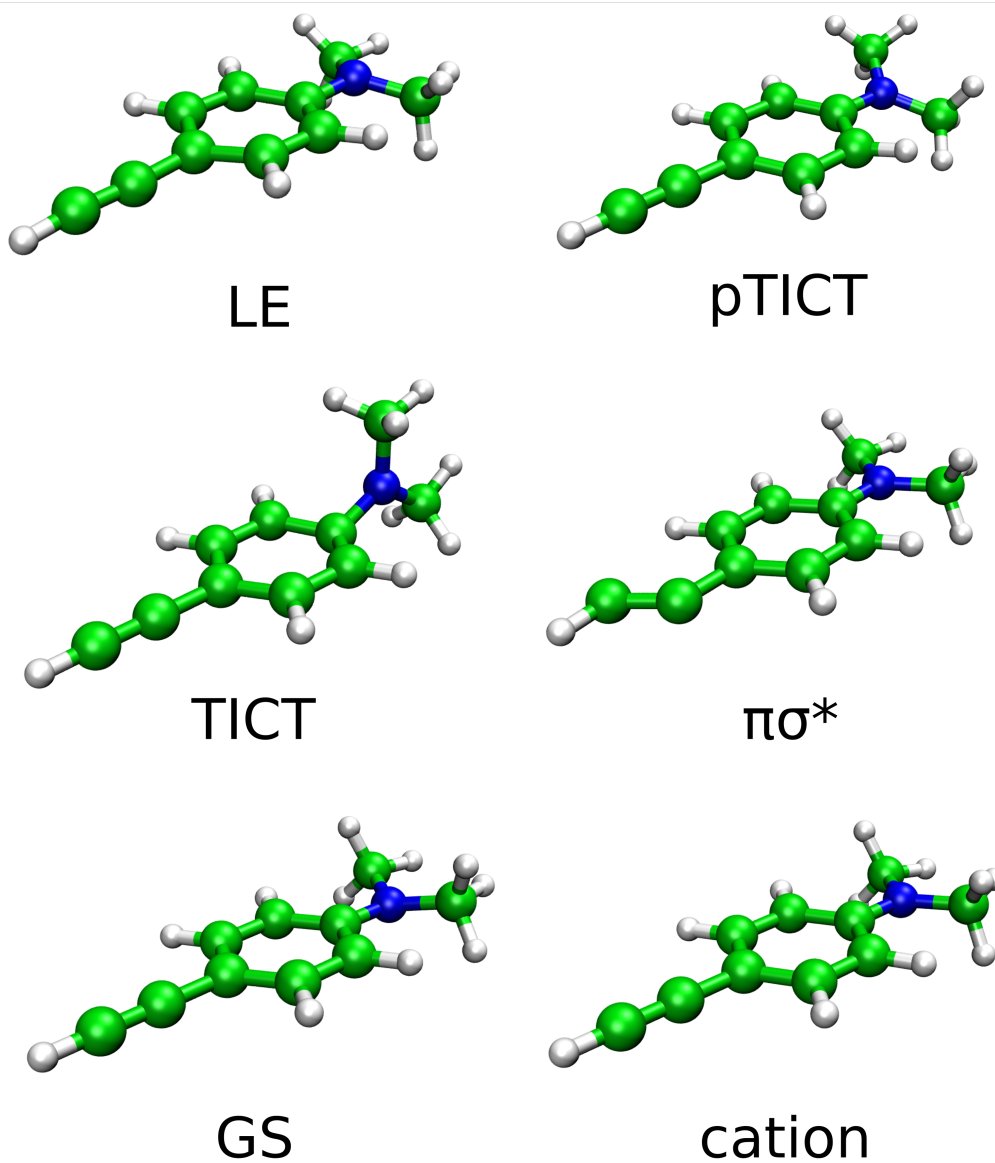


Fig. S3: Optimized structures for the neutral (GS) and cationic ground states as well as for the excited state isomers of DMABE at the TDDFT/ ω B97XD/aug-cc-pVDZ level of theory.

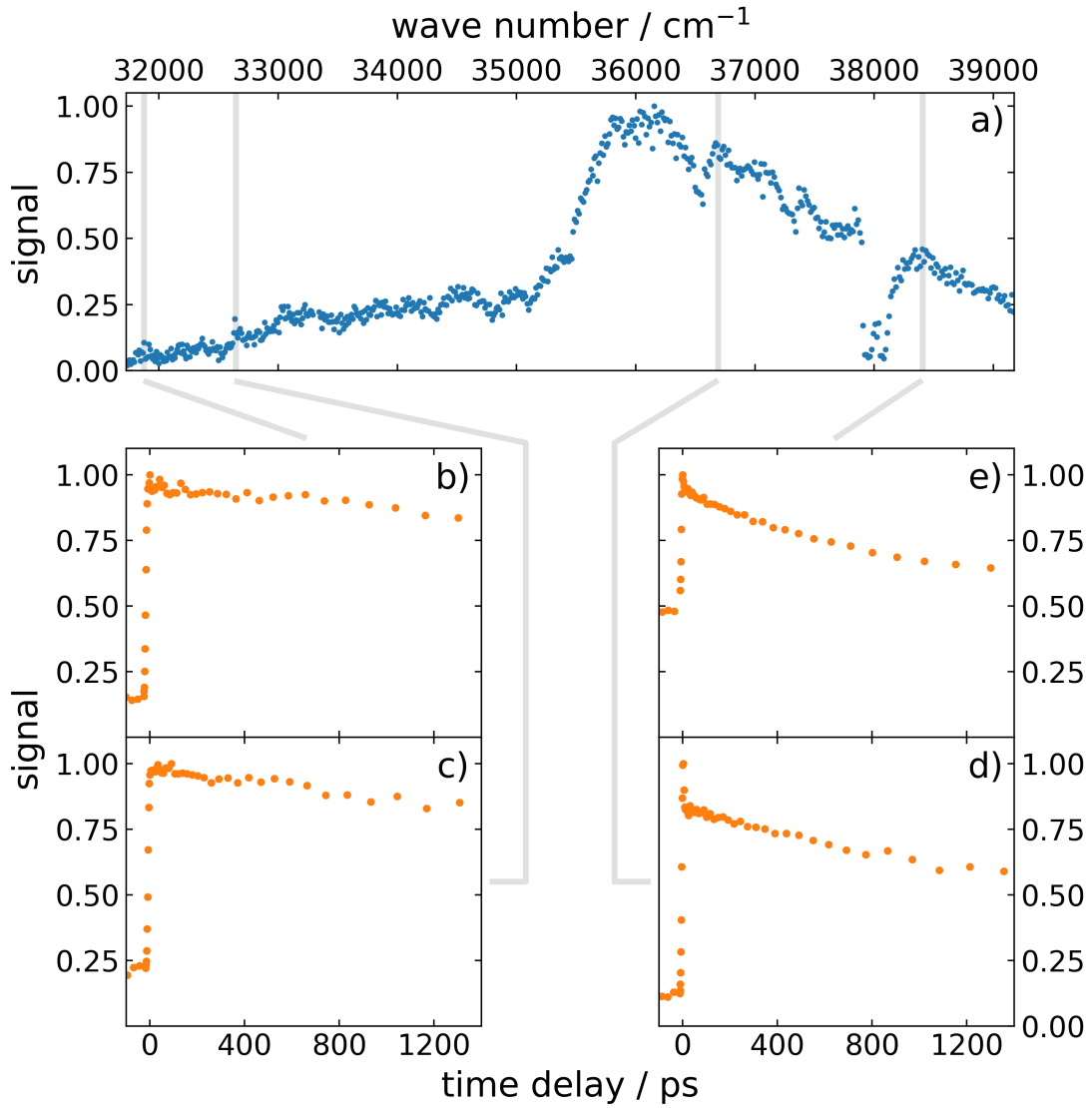


Fig. S4: (a) One-color REMPI of DMABE as presented in Fig. 2a in the main text. Time-delay traces recorded at the S_1 origin (31854 cm^{-1}) (b), at $+772 \text{ cm}^{-1}$ (c), at $+4816 \text{ cm}^{-1}$ (d) and at $+6534 \text{ cm}^{-1}$ (e).

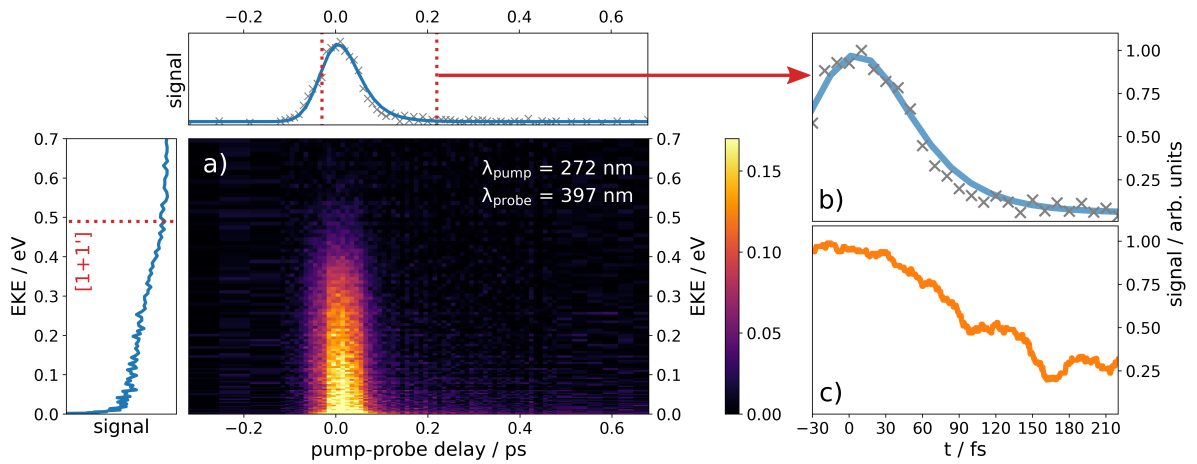


Fig. S5: Figure 6 of the main paper with the 397 nm probe time-resolved photoelectron spectrum (panel a) plotted with a perceptually uniform colormap.

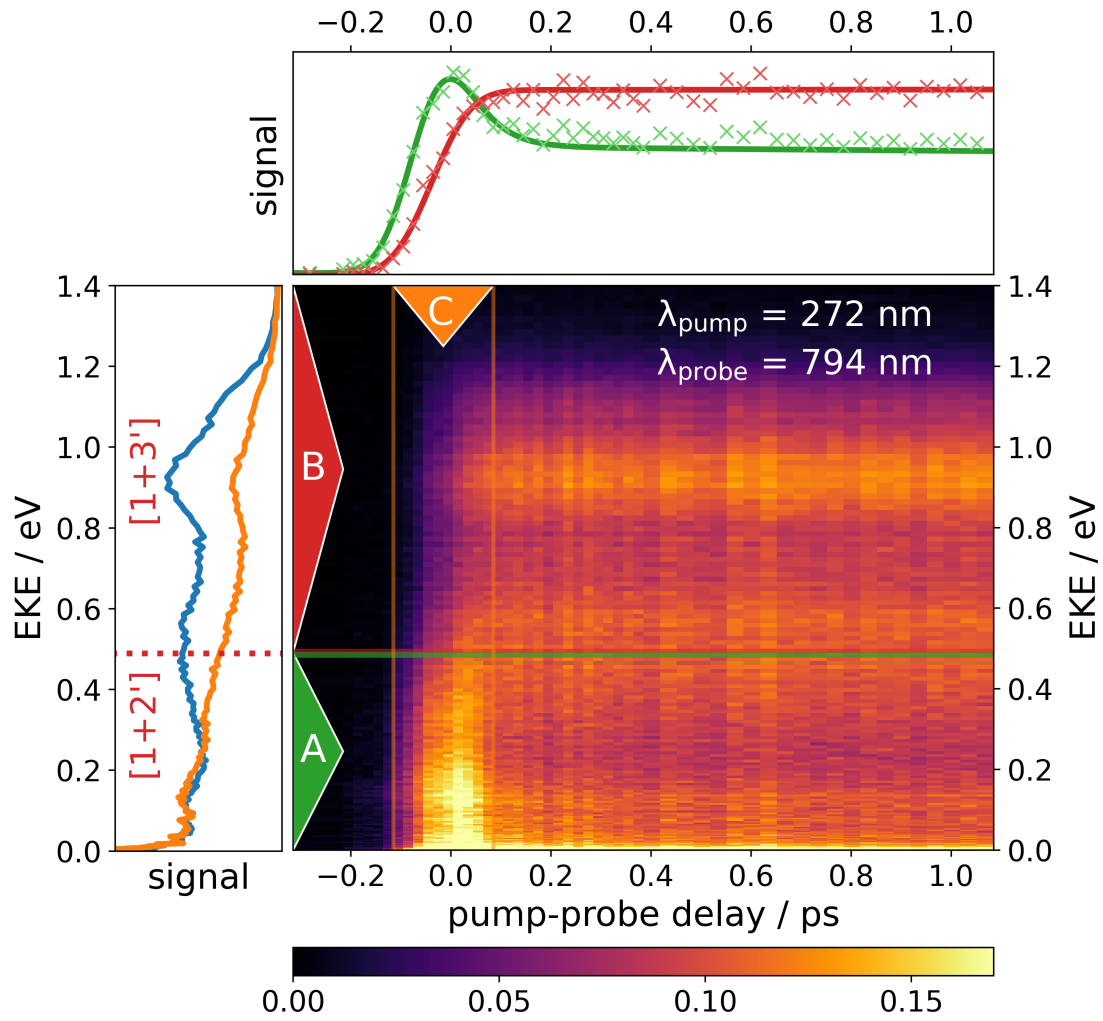


Fig. S6: Figure 7 of the main paper with the 794 nm probe time-resolved photoelectron spectrum (middle panel) plotted with a perceptually uniform colormap.

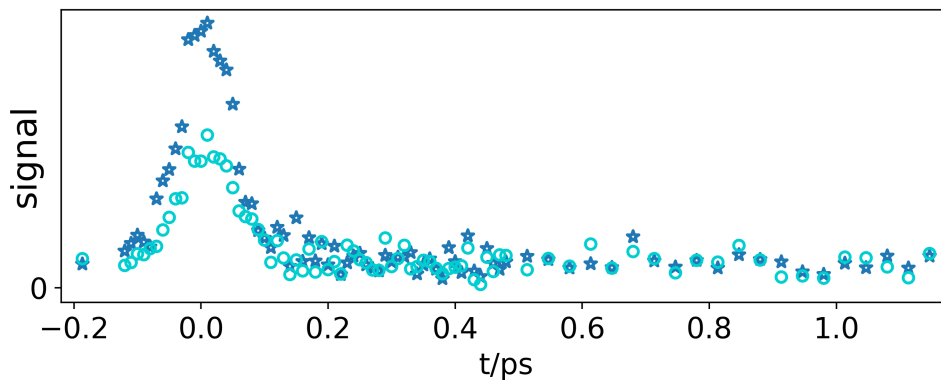


Fig. S7: Total time-dependent electron signal obtained from TRPES experiments employing 272 nm pump and 397 nm probe for orthogonal (open circles) and parallel laser polarization (stars). The rotationally averaged data are displayed in Fig. 6 of the main paper and Fig. S5.

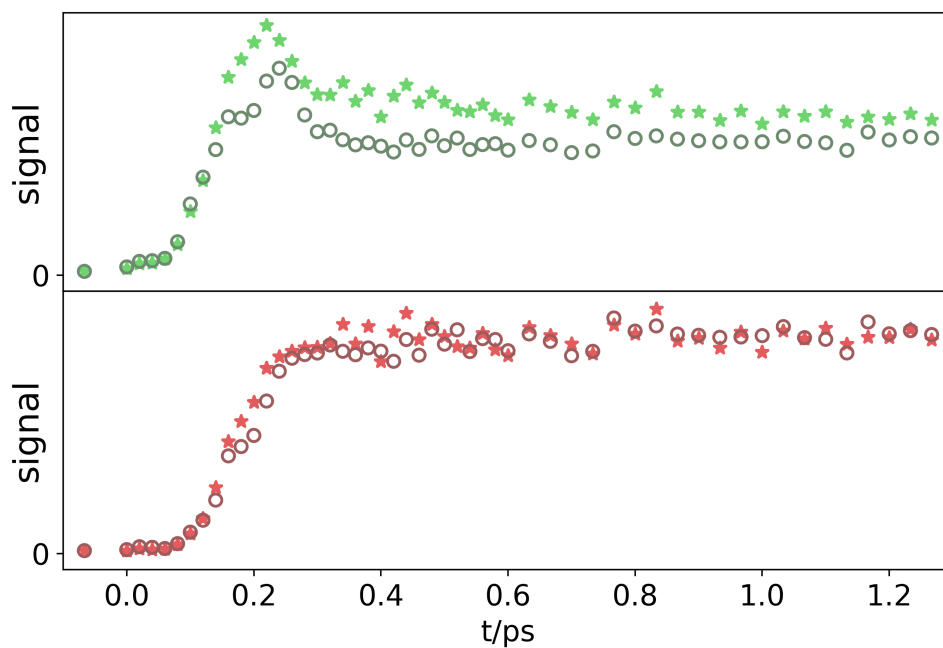


Fig. S8: Total time-dependent electron signal obtained from TRPES experiments employing 272 nm pump and 794 nm probe for orthogonal (open circles) and parallel laser polarization (stars) in the energy regions A (upper panel) and B (lower panel) as defined in Fig. S6. The rotationally averaged data are displayed in Fig. 7 of the main paper and Fig. S6.