Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A time-resolved photoelectron imaging study on isolated tolane: Observation of the biradicalic ^1A_u state.

Marco Flock, Lea Bosse, Dustin Kaiser, Bernd Engels and Ingo Fischer*

Institute of Physical and Theoretical Chemistry, University of Würzburg, 97074 Würzburg, Germany, e-mail: ingo.fischer@uni-wuerzburg.de

Tab. S1 xyz-coordinates of the optimised linear ground state tolane structure ((u)ωB97xD/def2TZVPP), values given in Å. E = -539.4547104 a. u. and $S^2 = 0$.

Atom	X	Y	Z
C	0.00004500	1.20041000	-4.12026700
C	0.00006400	1.20409800	-2.73652600
C	0.00001300	-0.00015200	-2.02885600
C	-0.00005700	-1.20420700	-2.73685600
C	-0.00007700	-1.20013200	-4.12059400
C	-0.00002600	0.00023600	-4.81623300
C	0.00008500	2.13901900	-4.65823200
C	0.00012000	2.13753400	-2.19062600
C	-0.00009700	-2.13778800	-2.19120600
H	-0.00013200	-2.13859500	-4.65881100
H	-0.00004100	0.00038900	-5.89801000
H	0.00003400	-0.00043100	-0.60153800
H	0.00005200	-0.00021300	0.60151600
H	-0.00005200	1.20412600	2.73658200
C	-0.00007900	1.20037500	4.12032500
C	-0.00003200	0.00016900	4.81623800
C	0.00004300	-1.20016900	4.12054500
C	0.00007000	-1.20417800	2.73680500
C	0.00002300	-0.00009700	2.02885300
H	-0.00008800	2.13758700	2.19072600
H	-0.00013700	2.13896200	4.65832800
H	-0.00005300	0.00027300	5.89801500
H	0.00008000	-2.13865400	4.65872100
H	0.00012800	-2.13774400	2.19112500

Tab. S2 xyz-coordinates of the optimised *trans-bent* cationic tolane structure ((u)ωB97xD/def2TZVPP), values given in Å. E = -539.1071841 a. u. and S^2 = 0.789924.

Atom	X	Y	Z
C	-0.00010000	0.45478400	-0.49811800
C	-0.00009600	-0.45479500	0.49812000
C	-0.00000100	0.20399200	-1.90114800
C	-0.00002800	-0.20399500	1.90114900
C	0.00027100	1.28958900	-2.79696500
C	0.00034700	1.08173000	-4.16158000
C	0.00007300	-0.21481600	-4.66210400
C	-0.00022500	-1.30564700	-3.79802700
C	-0.00022100	-1.10323300	-2.43457500
H	0.00040100	2.28977200	-2.38505200
H	0.00060100	1.92371400	-4.84055700
H	0.00009200	-0.37756300	-5.73223500
H	-0.00046400	-2.31079700	-4.19855400
H	-0.00037300	-1.93344300	-1.74147000
C	0.00021900	-1.28958900	2.79696900
C	0.00026400	-1.08172600	4.16158500
C	-0.00000600	0.21482200	4.66210300
C	-0.00027800	1.30564900	3.79802000
C	-0.00025300	1.10323100	2.43457000
H	0.00035900	-2.28977300	2.38506000
H	0.00049500	-1.92370900	4.84056400
H	-0.00000600	0.37757600	5.73223300
H	-0.00051100	2.31080000	4.19854500
H	-0.00038700	1.93344000	1.74146300

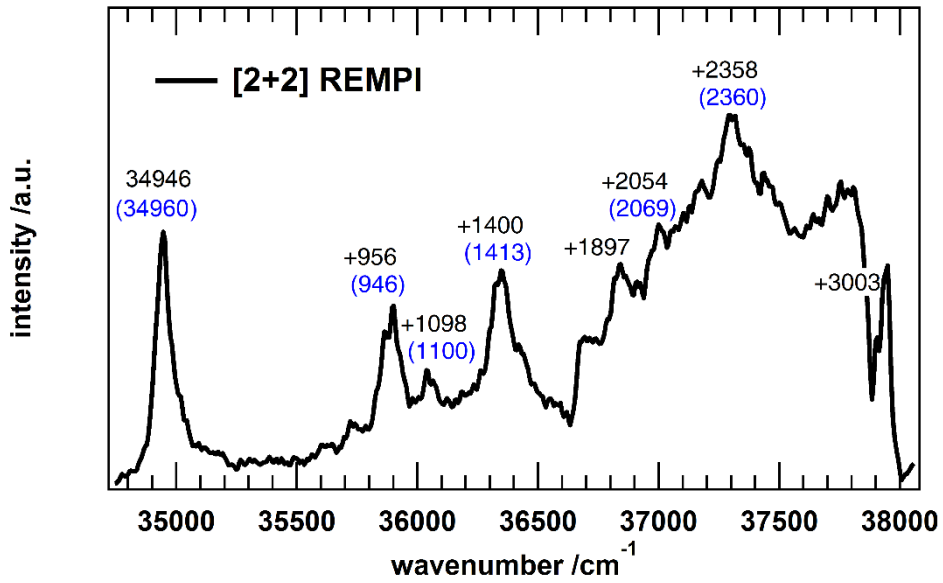

Fig. S1 [2+2] REMPI spectrum of tolane in the region of the lowest excited singlet states. Blue values in parentheses were taken from previous work by Okuyama *et al*.[1]

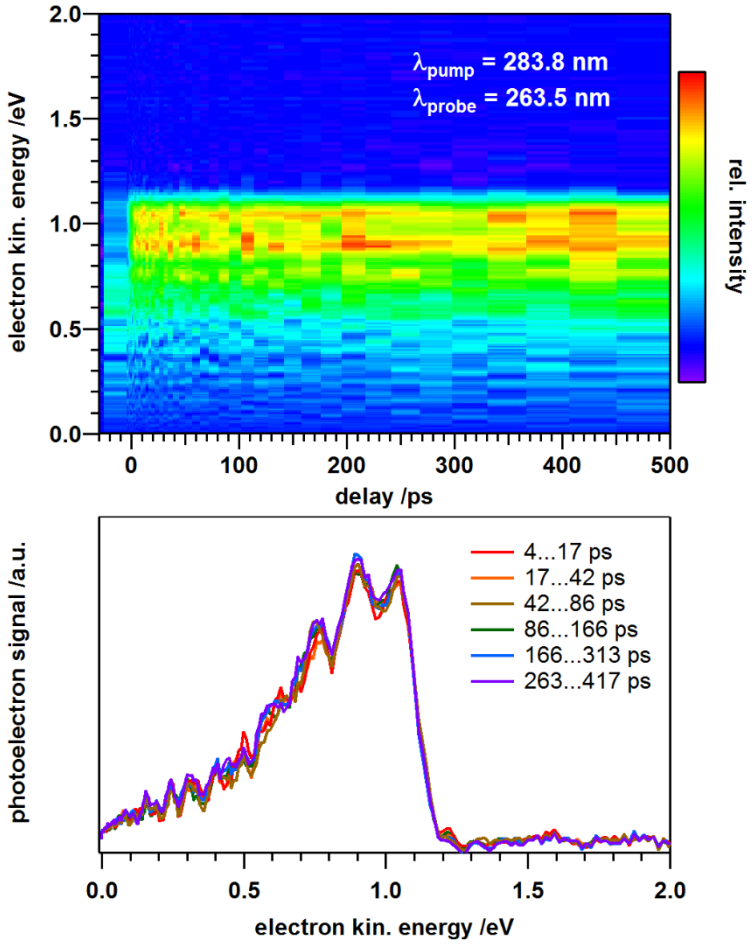

Fig. S2 Transient photoelectron map at an excitation wavelength of 283.8 nm (B_{1u} origin) and a probe wavelength of 263.5 nm. One-colour signals before time zero were subtracted in order to obtain the pure transient signal. The lower trace shows photoelectron spectra at different delay intervals. Only a weak time-dependence can be observed due to the ns lifetime of the B_{1u} origin band.

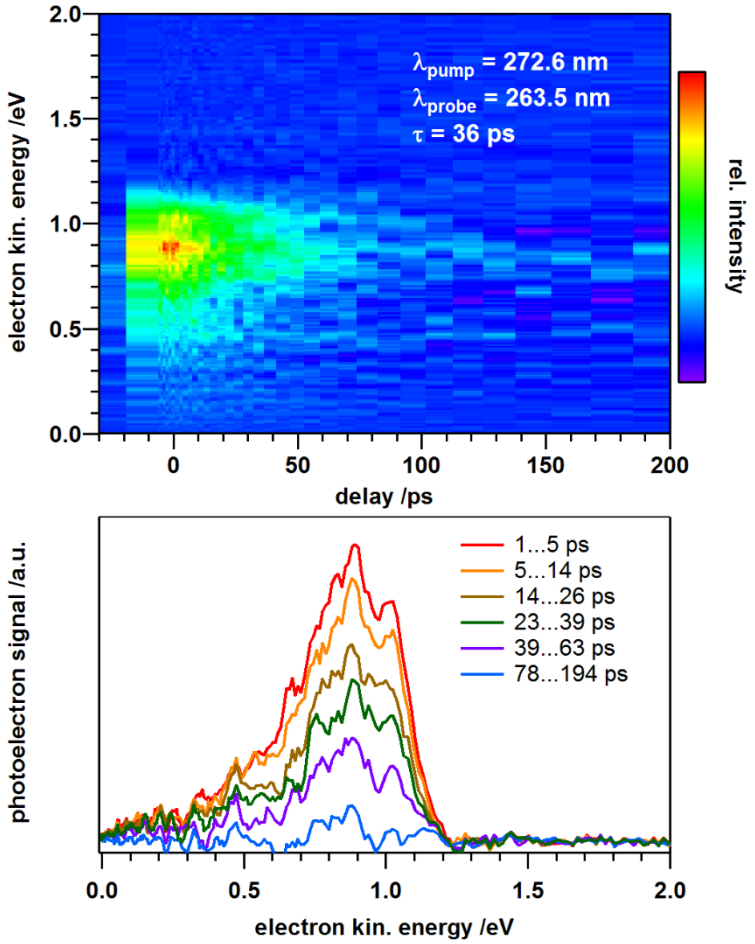

Fig. S3 Transient photoelectron map at an excitation wavelength of 272.6 nm (B_{1u} origin +1448 cm^{-1}) and a probe wavelength of 263.5 nm. One-colour signals before time zero were subtracted in order to obtain the pure transient signal. The lower trace shows photoelectron spectra at different delay intervals. The transient signal decays to zero monoexponentially (τ = 36 ps).

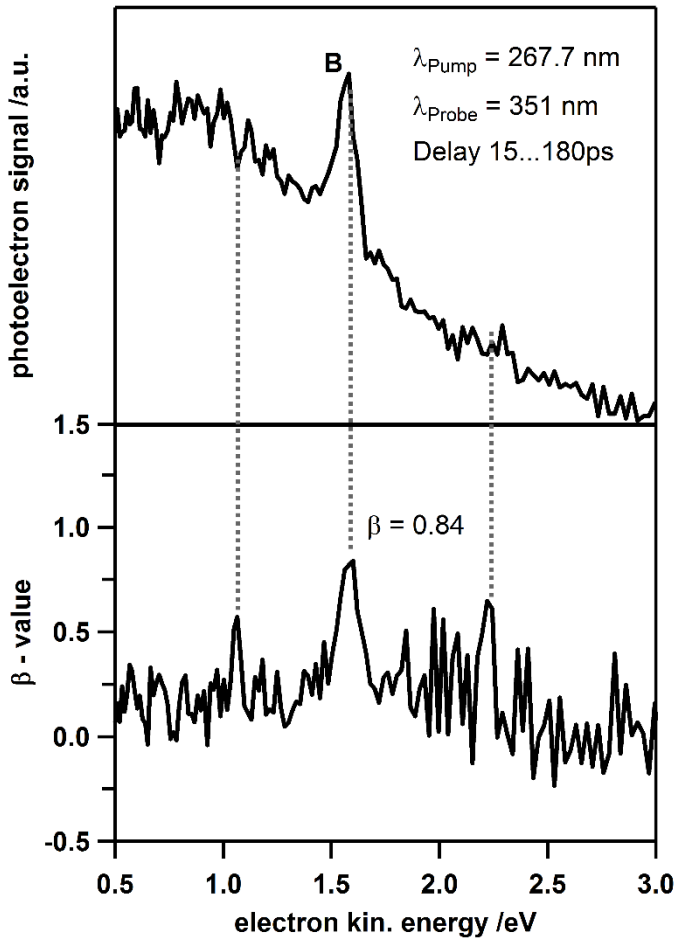

Fig. S4: Photoelectron angular distribution, showing the β-parameter in the delay range from 15 to 180 ps as a function of electron kinetic energy at an excitation wavelength of 267.7 nm (B_{1u} origin +2120 cm^{-1}) and a probe wavelength of 351 nm. In the region of peak B at 1.57 eV a positive anisotropy with β = +0.84 is observed. Two further peaks with a positive β are discernible at around 1.1 eV and 2.2 eV.

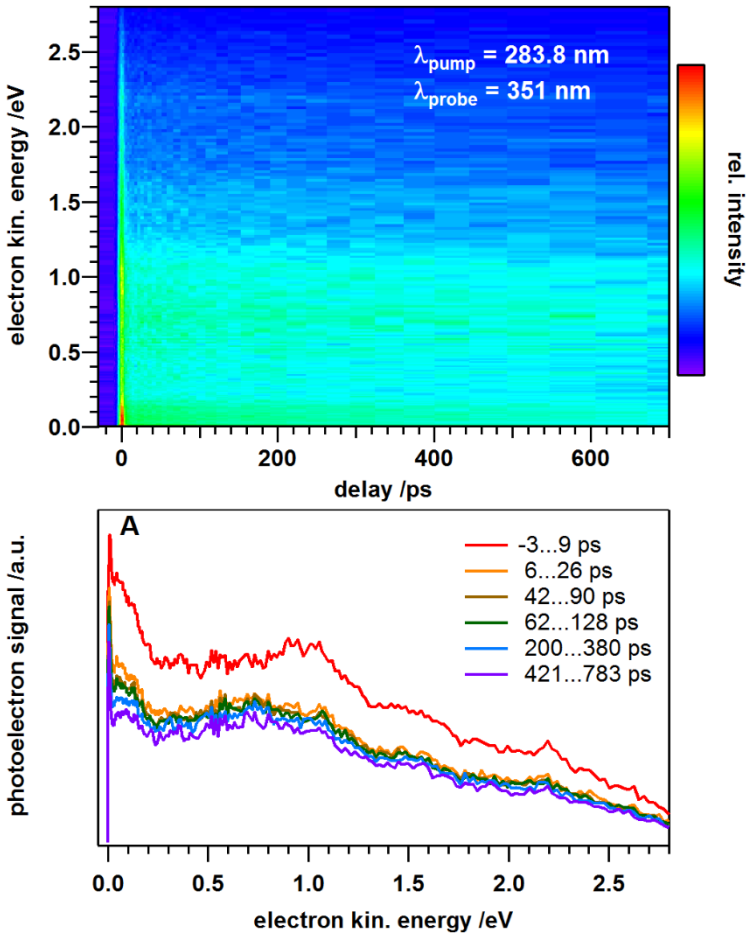

Fig. S5 Transient photoelectron map at an excitation wavelength of 283.8 nm ($^1B_{1u}$ origin) and a probe wavelength of 351 nm. One-colour signals before time zero were subtracted in order to obtain the pure transient signal. The lower trace shows photoelectron spectra at different delay intervals. Only Peak A originating from ionisation of the $^1B_{1u}$ origin with a ns lifetime is observed. Peak B is absent, demonstrating that it does not originate from ionisation of the $^1B_{1u}$ state.

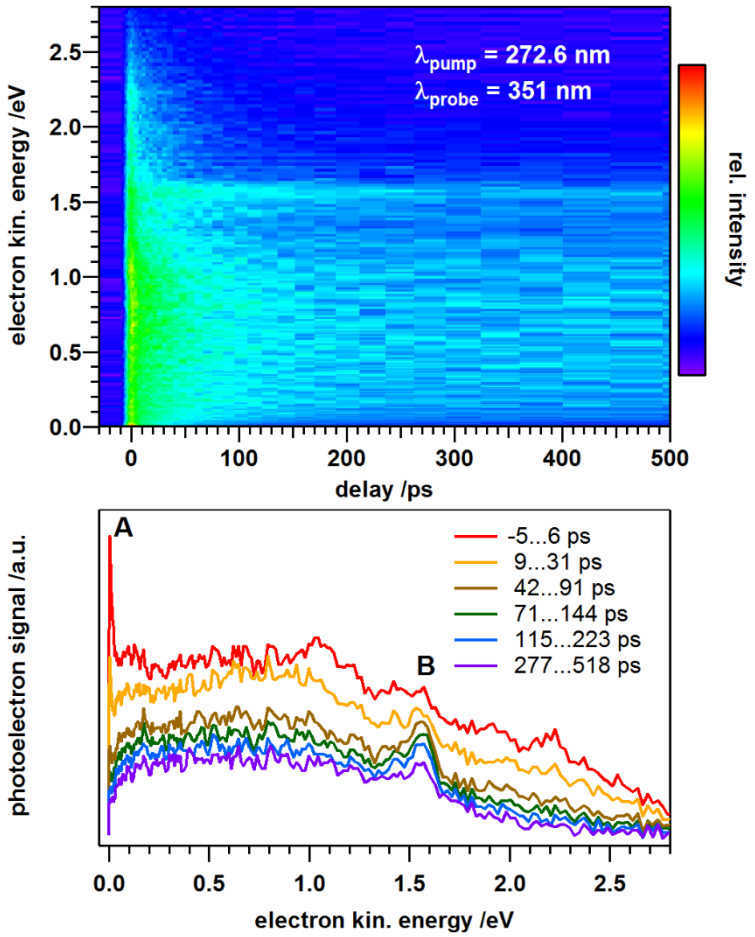

Fig. S6 Transient photoelectron map at an excitation wavelength of 272.6 nm (B_{1u} origin +1448 cm^{-1}) and a probe wavelength of 351 nm. One-colour signals before time zero were subtracted in order to obtain the pure transient signal. The lower trace shows photoelectron spectra at different delay intervals. The two peaks A and B appear at the same kinetic energy as in the spectra shown in Figures 5 and 6 (main paper) recorded at 267.7 nm.

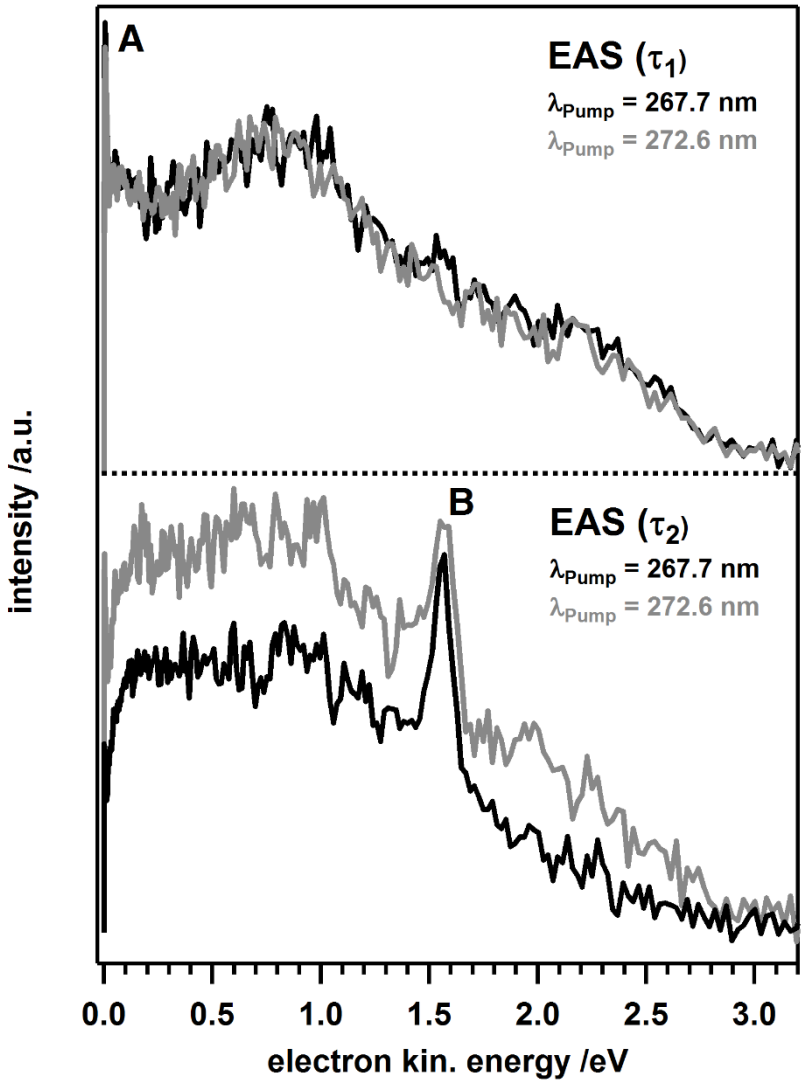

Fig. S7 EAS of time constants τ_1 and τ_2 at different excitation wavelengths (272.6 nm, +1448 cm^{-1} and 267.7 nm, +2120 cm^{-1}) and 351 nm probe wavelength. Despite the different excitation energy, peaks A and B appear at same electron kinetic energies.

Notes and references

1. K. Okuyama, T. Hasegawa, M. Ito and N. Mikami, *J. Phys. Chem.* 1984, **88**, 1711-1716.