Supporting Material for: Ultrafast photochemistry of free-base porphyrin: A theoretical investigation of $B \rightarrow Q$ internal conversion mediated by dark states

Konstantin Falahati[1], Carsten Hamerla[1], Miquel Huix-Rotllant[2], and Irene Burghardt[1]

[1] *Institute of Physical and Theoretical Chemistry, Goethe University Frankfurt, Max-von-Laue-Str. 7, 60438 Frankfurt/Main, Germany*

[2] *Aix Marseille Univ, CNRS, ICR, 13013 Marseille, France*

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1 Optimized Cartesian Coordinates of Conical Intersection Structures

The essential mechanistic analysis is centered on static chemical calculations revealing potentially accessible photochemical pathways. To this end conical intersection searches have been conducted relying on the branching-plane update method. All structures were obtained at the TDA-BH&HLYP/6-31G* level of theory with the GAMESS program package1. The obtained structures reveal a consistent mechanistic scenario indicating a photochemical route relying predominantly on in-plane motion of the porphine plane. Therefore the energetically unfavorable pyrrolic out-of-plane bending is effectively circumvented.

- xyz coordinates of the $S_2/S_1(N_{xy}/Q_x)$ conical intersection:

```
C -2.8289603 1.1818018 -0.0002194
C -4.2336241 0.8206506 -0.0015097
C -4.3333840 -0.5156629 -0.0004394
H -5.0321082 1.5387505 -0.0031808
C -2.9937876 -1.0695464 0.0011526
H -5.2231015 -1.1165465 -0.0013183
N -2.1299720 0.0171571 0.0009413
H -1.1248025 -0.0609083 0.0025000
N 0.0661269 1.9931136 0.0005554
N -0.0647889 -1.9807128 0.0001508
N 2.1274058 -0.1205880 0.0003658
C 1.1665655 2.7730389 0.0005584
C 0.8123046 4.1764128 0.0002163
C -0.5376217 4.2202128 -0.0000990
C -0.9812654 2.8425739 0.0000022
C -2.3285748 2.4605489 -0.0006751
C 2.4858074 2.3051209 0.0010980
C 2.9022035 0.9956598 0.0010198
C 4.2787949 0.5427206 0.0009248
C 4.2898606 -0.7979538 -0.0006515
C 2.9171441 -1.2618098 -0.0011210
C 1.0013613 -2.8041022 -0.0017137
C 2.4429369 -2.5099130 -0.0028206
C 0.6584815 -4.1136718 -0.0007278
C -0.9276119 -4.0614981 0.0017639
C -1.1834347 -2.7329813 0.0015261
C -2.6032759 -2.3455321 0.0021641
H -3.3389884 -3.1284408 0.0026042
H -1.5896418 -4.9081114 0.0031909
H 1.2634670 -5.0023263 -0.0014863
H 3.1258087 -3.3391600 -0.0041630
H 5.1233609 1.2060653 0.0018054
H 5.1376981 -1.4564878 -0.0014284
H 1.1194260 -0.1306769 -0.0003887
```

```
H 3.2664651 3.0485184 0.0010706
H -1.1776552 5.0841109 -0.0005773
H 1.5069676 4.9971926 -0.0000986
H -3.0595926 3.2529818 -0.0010222
```

- xyz coordinates of the $S_3/S_2(N_{xy}/Q_y)$ conical intersection

```
C 3.4817048 -0.2827392 -0.0020687
C -3.5578389 0.2531034 -0.0014950
C 3.7073987 2.2369356 0.0003646
C -3.2993463 2.7300762 -0.0004504
C 3.2597768 -2.7911127 0.0002994
C -3.7149109 -2.2606937 0.0006380
C 2.7162690 -1.4564335 -0.0020196
C -3.0318934 -0.9859650 -0.0024286
C 2.9772499 0.9969977 -0.0016546
C -2.7784180 1.4804254 -0.0006975
C 2.1984525 -3.6290694 0.0011296
C -2.7845262 -3.2364897 0.0016065
C 2.8189896 3.2495137 0.0008609
C -2.1225283 3.6606129 0.0015450
C 1.4827692 2.6920209 -0.0004465
C -1.0269957 2.8702768 0.0010828
C 1.0220156 -2.7954186 -0.0011361
C -1.4796948 -2.6316308 -0.0014295
C 0.3307354 3.3841315 0.0012953
C -0.2805441 -3.3062543 0.0000146
H 4.7792972 2.3066770 0.0019716
H -4.3323549 3.0263418 -0.0019372
H 4.5548505 -0.3844136 -0.0010122
H -4.6298162 0.3549446 -0.0001683
H 4.3051189 -3.0419038 0.0021340
H -4.7829223 -2.3738371 0.0024912
H 2.1972395 -4.7037868 0.0035733
H -2.9479112 -4.2980918 0.0041412
H 3.0226832 4.3041291 0.0023547
H -2.1664048 4.7335162 0.0041988
H 0.9397065 0.6190019 -0.0029489
H -0.9575520 -0.5949047 -0.0032661
H 0.4130982 4.4572677 0.0024271
H -0.3627894 -4.3805558 0.0033784
N 1.3617645 -1.4865538 -0.0029009
N -1.6825530 -1.2861227 -0.0053989
N 1.6556619 1.3229653 -0.0023334
N -1.4011958 1.5415838 0.0003050
```

- xyz coordinates of the $S_3/S_2(B/Q)$ conical intersection

```
C -0.3730337 4.0528069 -0.6675438
C -0.3733271 4.0543507 0.6676406
C -1.5192096 -2.8811371 -0.6802306
C -1.5190766 -2.8808432 0.6795805
C -0.1713369 -2.6965306 -1.1231617
C -0.1712762 -2.6958969 1.1220787
C -0.2061475 2.6779738 -1.1329167
C -0.2065077 2.6807809 1.1364800
C 0.3458813 -2.4799381 -2.4508002
C 0.3460492 -2.4769470 2.4485773
C -0.0960568 2.2884998 -2.4191584
C -0.0970061 2.2907975 2.4227994
C 0.3752489 -1.1991981 -2.9273006
C 0.3765641 -1.1963403 2.9234640
C 0.6432035 -0.7481686 -4.2708960
C 0.6431576 -0.7471461 4.2683198
C 0.1287941 0.9443645 -2.8836817
C 0.1288534 0.9454924 2.8816876
C 0.4692635 0.5956547 -4.2484054
C 0.4686848 0.5965354 4.2466868
H -0.4643553 4.8951031 -1.3283040
H -0.4636089 4.8985568 1.3258355
H -2.3522032 -2.9537480 -1.3499057
H -2.3516260 -2.9540340 1.3497789
H 0.5774877 -3.3281368 -3.0733793
H 0.5721710 -3.3226309 3.0762238
H -0.1422121 3.0667470 -3.1624742
H -0.1430145 3.0626275 3.1727863
H 1.5676072 -2.4090857 -0.0006406
H 0.8950992 -1.3759436 -5.1052300
H 0.8957944 -1.3754584 5.1023839
H 0.5662920 1.2899750 -5.0629814
H 0.5663558 1.2902937 5.0618115
H -0.0392508 0.9036155 0.0028833
N 0.5961971 -2.6584972 -0.0005588
N -0.1421162 1.9035225 0.0023019
N 0.0754691 -0.1217495 -2.1104700
N 0.0777273 -0.1190354 2.1067195
```

- xyz coordinates of the $S_5/S_6(B_x/B_y)$ conical intersection

```
C -2.8232139425   1.2203132326   0.0035561443
C -4.2142817168   0.8103369494   0.0015320412
C -4.2580319154  -0.5302829879  -0.0007454865
H -5.0353096134   1.5035476790  -0.0024322033
C -2.8987276844  -1.0324054122   0.0075936260
H -5.1230129131  -1.1679408857  -0.0041572875
```

```
N -2.0811567672   0.0678237923   0.0134152037
H -1.0730348163   0.0330942415   0.0247938487
N 0.0616638517   2.0202067078  -0.0064819504
N -0.0665796223  -2.0143897935   0.0002313096
N 2.0856141729  -0.0740625524   0.0107196946
C 1.1628914689   2.8082744138  -0.0088293042
C 0.8199177309   4.2065627856  -0.0057418428
C -0.5450939225   4.2489453332  -0.0062794513
C -0.9649254809   2.8712568769  -0.0084956907
C -2.3524729085   2.4880667014  -0.0009895763
C 2.4976101300   2.3348095888  -0.0025659686
C 2.8946649863   1.0296163821   0.0085239850
C 4.2527833732   0.5331353147   0.0091191084
C 4.2125862827  -0.8121074247   0.0036924236
C 2.8274604284  -1.2232761949  -0.0023857717
C 0.9805046264  -2.8777412917  -0.0086852974
C 2.3441732394  -2.5002267131  -0.0160149791
C 0.5445881264  -4.2464180344  -0.0014252305
C -0.8199382762  -4.1967567184   0.0029868353
C -1.1471684398  -2.7933359531   0.0011950626
C -2.5074778091  -2.3243471910   0.0033542698
H -3.2742018911  -3.0806228694   0.0007771072
H -1.5202123609  -5.0107249181   0.0007814700
H 1.1843630276  -5.1081903621  -0.0060739080
H 3.0718567280  -3.2957493546  -0.0173119970
H 5.1214860193   1.1662137671   0.0165287081
H 5.0398828104  -1.4990420566  -0.0001903207
H 1.0770188848  -0.0472559035   0.0018976029
H 3.2795371764   3.0776293560  -0.0044819556
H -1.1918821918   5.1066654405  -0.0012288522
H 1.5147875819   5.0241993379  -0.0006820661
H -3.0766723726   3.2841757161  -0.0055303007
```

2 DFT Benchmarks and Additional Computational Considerations

Throughout this work a variety of DFT functionals was screened regarding geometric and excited state properties of the free-base porphine molecule. For the benchmark calculations the Gaussian092 program package was used as cited in the main paper.

The influence of the basis set quality is depicted for the B3LYP, BP86 and CAM-B3LYP functional in combination with the 6-31G* and the SVP basis sets.

Additionally, the PCM solvation model was utilized to explore environmental stabilization or alteration of mechanistic details in the presence of benzene.

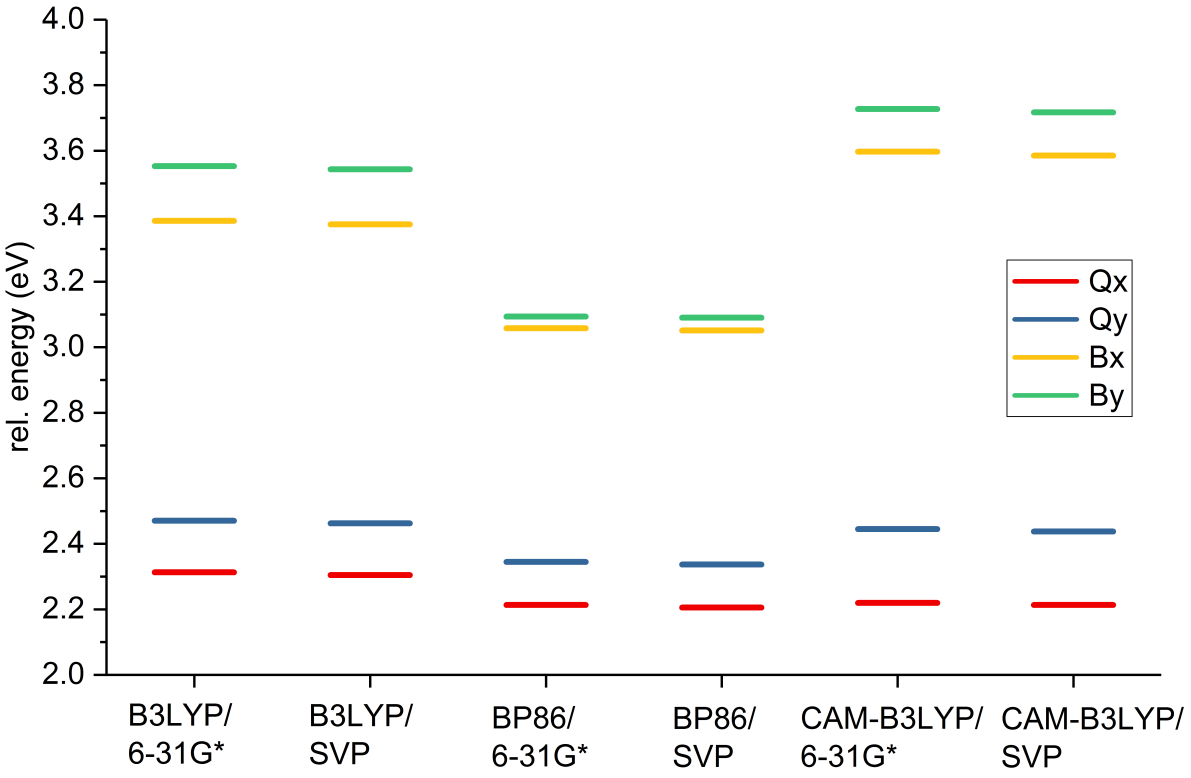

Figure S1 – Q_x, Q_y, B_x, and B_y state energies in eV displayed for TDDFT calculations with various functionals

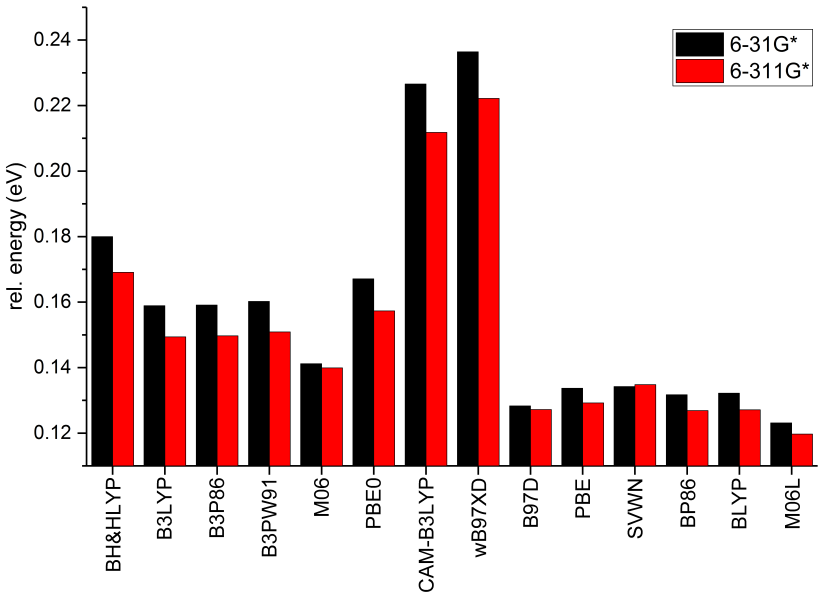

Figure S2 – Depiction of the Q state energy gap in eV for different functionals (6-31G* and 6-311G* basis sets).

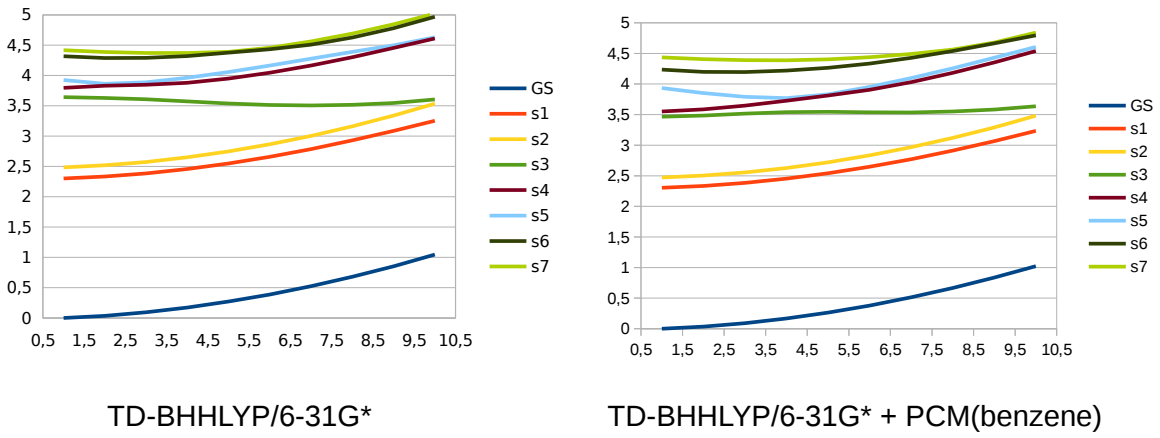

Figure S3 – The marginal influence of a PCM solvation model (benzene) is demonstrated for the $S_3/S_2(N_{xy}/Q_y)$ conical intersection. To this end a one-dimensional potential cut without PCM (left) and with PCM solvation model (right) along a linear interpolation coordinate is displayed connecting the Franck-Condon minimum structure with the CI structure, all relative energies in eV.

3 Multiconfigurational Assessment and Comparison to TDDFT

To evaluate the reliability of the employed TDDFT methodology multiconfigurational calculations[3, 4] were performed. As can be inferred from the data below, qualitative and semi-quantitative agreement is obtained. Especially the relative topologies of the potential surfaces of states S_2, S_3 and S_4 are mapped comparably well, a fact that is crucial for the subsequent non-adiabtic dynamics simulation.

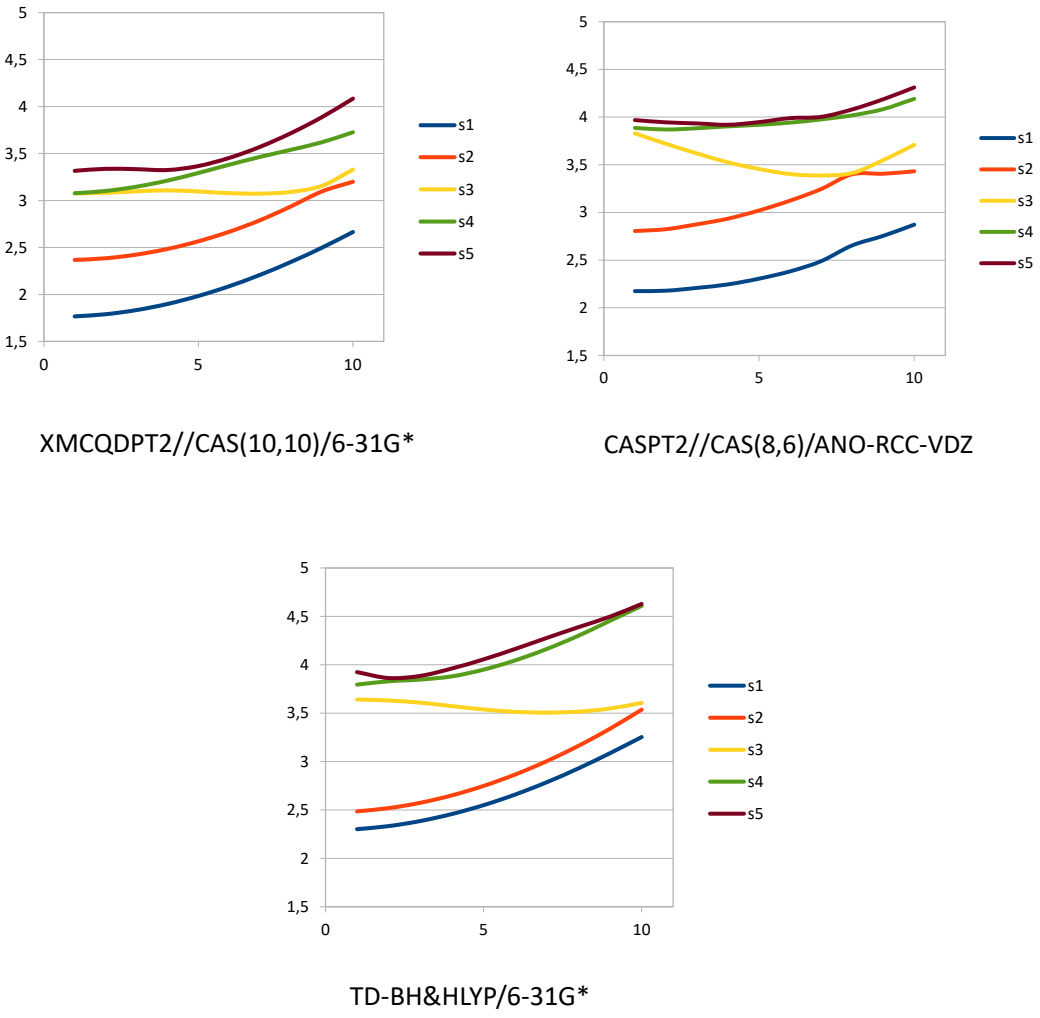

Figure S4 – Benchmark of TDDFT against multiconfigurational treatment (PES scans)

Table S1 – Active space composition for the multiconfigurational approaches pursued in this study

CAS type	composition	CI roots
CAS(4,4)	$5b_{1u}2a_u4b_{3g}4b_{2g}$	4
CAS(8,6)	$4b_{1u}3b_{3g}5b_{1u}2a_u4b_{3g}4b_{2g}$	10
CAS(10,10)	$3b_{2g}4b_{1u}3b_{3g}5b_{1u}2a_u4b_{3g}4b_{2g}3a_u6b_{1u}5b_{3g}$	15

Table S1 displays the different active spaces utilized in this study. The (4,4) and (8,6) active spaces correspond to the Gouterman space and the extended Gouterman space shown in Figure 1 of the manuscript. The XMCQDPT2 calculations necessitate a larger active space (here, (10,10)) to properly describe higher CI roots; specifically, 15 CI roots were included to converge the lowest five singlet states. (The (10,10) CAS additionally comprises the HOMO-4 as well as the LUMO+2, LUMO+3 and LUMO+4 orbitals.)

4 Non-Adiabatic Molecular Dynamics Simulations

Summed populations for the "B band" as well as for "B band" and "Q band" are displayed for the sake of comparability to experimental studies. The data has been displayed to complement the graphical depiction in Fig. 5 of the main paper. Here the emphasis has been given to the "spectroscopic" bands in order to highlight qualitative and even satisfactory semi-quantitative agreement with experimental studies cited in the main text. The Newton-X program package[5, 6] has been used for the non-adiabatic surface-hopping dynamics simulations. Exponential fit of the B state population decay yields an approximate lifetime of 100 fs.

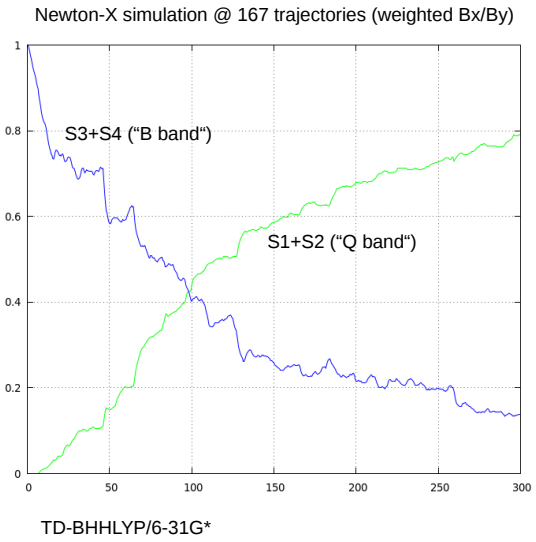

Figure S5 – State populations throughout the dynamics simulation, 167 trajectories, TDBH&HLYP/6-31G* level, weighted initial condition according to By/Bx ratio of oscillator strengths, B band and Q band summed.

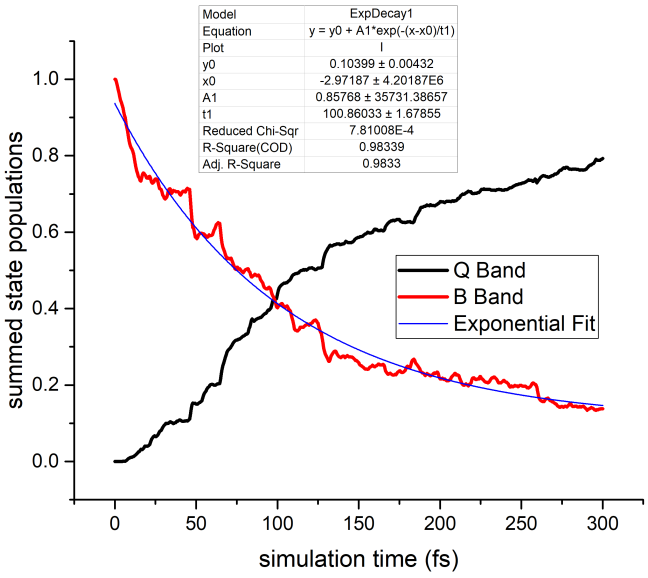

Figure S6 – Exponential fit of the B band state population decay displayed against the Q band rise. The lifetime τ is obtained to be approximately 100 fs.

References

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