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

Femtosecond photodecarbonylation of Photo-ODIBO studied by Stimulated Raman Spectroscopy and Density Functional Theory.

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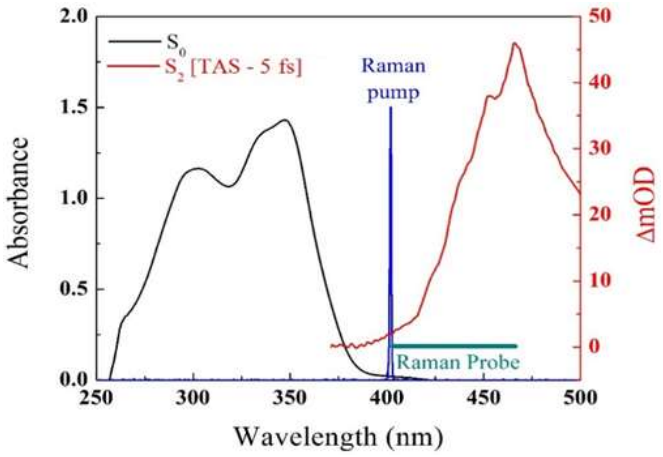
Supplementary Information

Contents

1. UV-VIS, Transient Absorption, and Raman Pump Spectra

Our previous transient absorption experiments (TA) showed that Photo-ODIBO has an excited state absorption (ESA) in the 370 nm to 500 nm wavelength range that overlaps with the Stokes probe wavelength range chosen for the FSRS study. Figure 1 shows the resulting spectra after 321 nm excitation, including the Raman pump wavelength selected. The ground state absorption spectrum of Photo-ODIBO is also shown. The 468 nm peak was attributed to S_2 absorption after 321 nm excitation. A global fit analysis of the TA electronic dynamics resulted in a 294 fs time constant immediately following excitation. Further analysis suggested that decarbonylation was initiated upon excitation to the S_2 excited state and also occurred within the 294 fs relaxation time.[1]



SI Figure 1: Steady state absorption (black) and transient absorption peak following 321 nm excitation of Photo-ODIBO (red). The Raman pump spectrum is also shown (blue). The dark cyan bar shows the probe wavelength (Raman probe) used.

2. DFT Calculations for Photo-ODIBO and ODIBO

Photo-ODIBO S_0, S_1 and S_2 Geometries

Photo-ODIBO S_0 Geometry

C	6.537122	-0.570992	-0.938949
C	6.431558	-1.955871	-1.146584
C	5.158196	-2.561168	-1.168986
C	4.001912	-1.814542	-0.979734
C	4.106279	-0.413021	-0.758888
C	5.377403	0.182922	-0.753668
C	2.922463	0.385421	-0.552343
C	0.470654	-0.538897	0.006908
C	0.696429	-1.918058	0.245109
C	-0.377277	-2.724526	0.621875
C	-1.660506	-2.184276	0.756606
C	-1.922986	-0.823415	0.514298
C	-0.831613	-0.023814	0.144016
C	1.577374	0.335979	-0.301832
O	1.945963	-2.462371	0.187660
C	2.197524	1.621956	-0.455080
O	7.480263	-2.786094	-1.337919
H	7.507685	-0.074708	-0.922599
H	5.108478	-3.638434	-1.345926
H	5.452656	1.261576	-0.594302
H	-0.189478	-3.782204	0.819964
H	-2.466660	-2.854024	1.058017
C	-3.326357	-0.199289	0.650903
H	-0.963597	1.044620	-0.041086
O	2.147452	2.829828	-0.476697
C	8.794385	-2.267197	-1.319451
C	-3.291586	0.910037	1.727808
C	2.648036	-2.479675	-1.066539
C	-4.385300	-1.238149	1.063513
C	-3.750706	0.411910	-0.705185
H	2.034640	-1.986867	-1.839727
H	9.467362	-3.119254	-1.483840
H	2.773585	-3.534452	-1.361885
H	9.036338	-1.801723	-0.347163
H	8.952204	-1.524414	-2.121925
H	-4.287793	1.369179	1.841010
H	-2.582897	1.711530	1.469780
H	-2.993711	0.501328	2.706826
H	-5.370577	-0.752539	1.144131
H	-4.159711	-1.688784	2.043291
H	-4.478476	-2.051567	0.325699
H	-4.754929	0.860750	-0.627684
H	-3.781989	-0.357863	-1.493441
H	-3.059212	1.202529	-1.035600

Photo-ODIBO S_1 Geometry

C	6.574209	-0.559913	-1.061644
C	6.474835	-1.960932	-1.148688
C	5.204065	-2.569401	-1.053859
C	4.048245	-1.829247	-0.865269
C	4.150751	-0.395319	-0.748620
C	5.430122	0.206032	-0.863870
C	2.961347	0.316073	-0.502013
C	0.448070	-0.462489	0.083387
C	0.681958	-1.862826	0.298852
C	-0.391778	-2.683638	0.605127
C	-1.696498	-2.166971	0.705898
C	-1.956959	-0.795264	0.510648
C	-0.874526	0.036908	0.204437
C	1.588077	0.301716	-0.234824
O	1.963625	-2.353161	0.328912
C	2.250562	1.529253	-0.392894
O	7.525250	-2.804467	-1.326920
H	7.539886	-0.059275	-1.140540
H	5.155039	-3.657643	-1.148731
H	5.520746	1.292395	-0.785717
H	-0.194906	-3.741756	0.794156
H	-2.504716	-2.856245	0.947531
C	-3.373256	-0.192171	0.631146
H	-1.031888	1.106450	0.048826
O	2.236108	2.759270	-0.412139
C	8.825985	-2.274039	-1.427762
C	-3.390939	0.854119	1.769284
C	2.696052	-2.513616	-0.891295
C	-4.436120	-1.261069	0.946020
C	-3.761715	0.492148	-0.700279
H	2.092059	-2.131462	-1.735128
H	9.504551	-3.127831	-1.559544
H	2.845025	-3.593570	-1.060990
H	9.119089	-1.723620	-0.514291
H	8.929800	-1.597685	-2.296606
H	-4.396740	1.294327	1.875394
H	-2.684771	1.677113	1.580584
H	-3.118535	0.394100	2.732841
H	-5.428933	-0.789165	1.017107
H	-4.240724	-1.764926	1.905852
H	-4.491745	-2.031818	0.160438
H	-4.774286	0.923703	-0.630963
H	-3.755597	-0.230727	-1.532198
H	-3.070226	1.308018	-0.961277

Photo-ODIBO S_2 Geometry

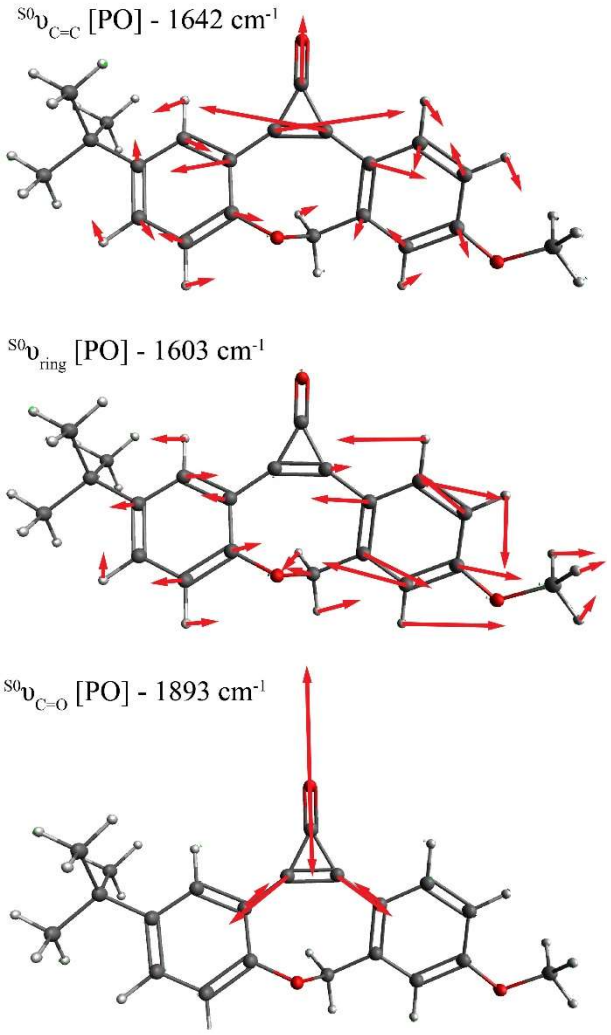
C	6.429604	-0.562504	-0.713827
C	6.325257	-1.969427	-0.909447
C	5.077406	-2.530849	-1.205705
C	3.925567	-1.745780	-1.290425
C	4.010433	-0.314703	-1.046951
C	5.304021	0.233898	-0.794162
C	2.840419	0.452518	-1.052737
C	0.399580	-0.574142	-0.527527
C	0.629520	-1.992581	-0.329886
C	-0.344184	-2.766349	0.358088
C	-1.572618	-2.233914	0.720693
C	-1.865834	-0.873925	0.461681
C	-0.851019	-0.084569	-0.141369
C	1.439954	0.337633	-0.916076
O	1.699065	-2.680844	-0.701579
C	2.010931	1.632161	-0.880862
O	7.381233	-2.829776	-0.861796
H	7.393124	-0.101545	-0.493767
H	5.036437	-3.605413	-1.404050
H	5.388357	1.310589	-0.626137
H	-0.106579	-3.818172	0.529548
H	-2.307484	-2.883789	1.193852
C	-3.202567	-0.226368	0.833626
H	-1.013169	0.986052	-0.277848
O	1.906591	2.835019	-0.745473
C	8.674670	-2.326649	-0.628276
C	-2.949192	0.906115	1.862161
C	2.643799	-2.329479	-1.776271
C	-4.190331	-1.232481	1.451708
C	-3.846966	0.374366	-0.441385
H	2.117425	-1.667486	-2.480389
H	9.355675	-3.189025	-0.648956
H	2.816010	-3.304510	-2.252989
H	8.756969	-1.834070	0.358526
H	8.987866	-1.607038	-1.407871
H	-3.905579	1.379729	2.137117
H	-2.289035	1.690740	1.463180
H	-2.488614	0.510583	2.780888
H	-5.137518	-0.724101	1.688873
H	-3.806370	-1.663260	2.389575
H	-4.422965	-2.058492	0.761241
H	-4.807355	0.849981	-0.184914
H	-4.042481	-0.407504	-1.192186
H	-3.209452	1.140736	-0.907515

Table 1: Bond lengths for Photo-ODIBO at the S_0, S_1, and S_2 optimized structures

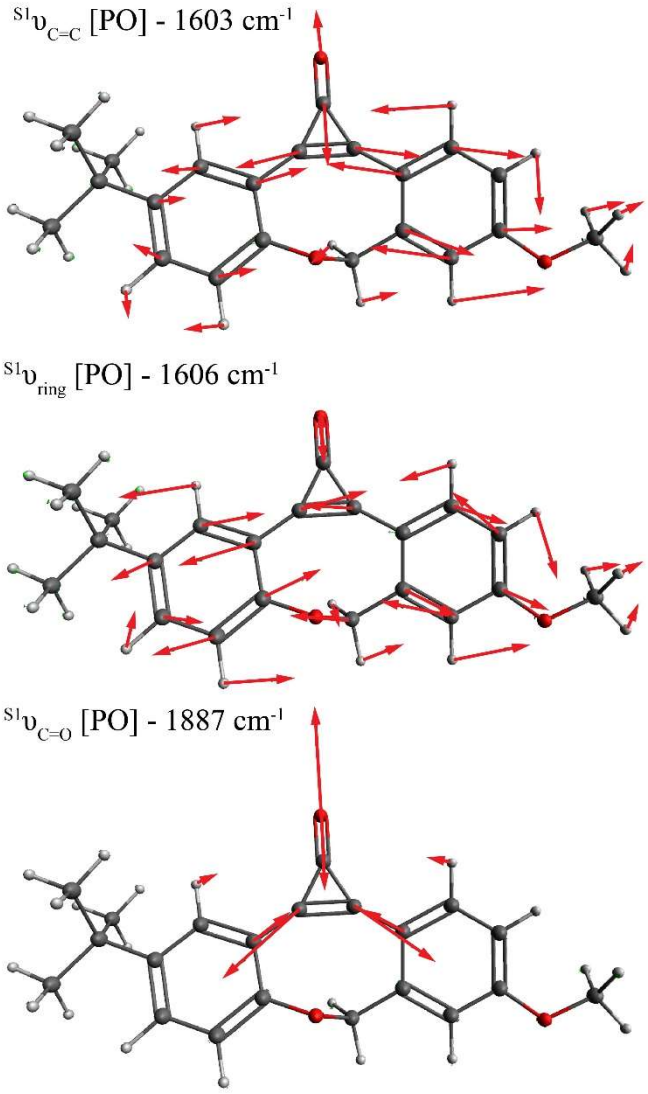
	Bond Lengths		
Bond	**S_0**	**S_1**	**S_2**
$C^7 = C^8$	1.369	1.399	1.412
$C^{23} = O^{25}$	1.209	1.230	1.215
$C^8 – C^{23}$	1.436	1.404	1.415
$C^7 – C^{23}$	1.437	1.410	1.452
$C^8 – C^{23} – C^7$ angle	56.9	59.6	59.0

Photo-ODIBO Raman Calculations

The S_0 and S_1 Raman modes below were computed on the ground-state and S_1 excited state at the same level of theory indicated in the manuscript. The red arrows indicate the direction of motion of the atoms and were scaled (X 1.5) for better visibility in the Avogadro software program. Mode assignments are based on the dominant activity for each calculated frequency.



SI Figure 2: Calculated Raman modes for S_0 Photo-ODIBO showing atomic displacements. Descriptions of the modes are also provided.



SI Figure 3: Calculated Raman modes for S_1 Photo-ODIBO showing atomic displacements.

Vibrational Mode Decomposition

S_2 Vibrational Modes (cm^{-1})	Decomposition
1870	+0.8785 (14.4%) BOND C23 O25 -0.6941 (11.4%) BOND C8 C23 -0.6360 (10.5%) BOND C7 C23 +0.3331 (5.5%) ANGLE C7 C23 C8 Shown Composition: 86.9% BOND, 13.1% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 53.4% BOND, 30.3% ANGLE, 0.1% OUT, 16.2% TOR
1605	Disperse Ring mode Largest Contribution: +0.5253 (4.3%) BOND C2 C3 Shown Composition: 0.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 32.4% BOND, 60.3% ANGLE, 0.2% OUT, 7.1% TOR
1599	Disperse Ring mode Largest Contribution: +0.5906 (4.3%) BOND C9 C13 Shown Composition: 0.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 32.4% BOND, 57.6% ANGLE, 0.2% OUT, 9.7% TOR
1575	-0.6951 (5.9%) BOND C5 C7 +0.6259 (5.3%) BOND C7 C8 Shown Composition: 100.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 37.3% BOND, 52.1% ANGLE, 0.3% OUT, 10.3% TOR

S_1Vibrational Mode (cm^{-1})	Decomposition
1887	-0.7768 (13.3%) BOND C23 O25 +0.7099 (12.2%) BOND C8 C23 +0.6907 (11.9%) BOND C7 C23 +0.4303 (7.4%) BOND C7 C8 -0.3691 (6.3%) BOND C8 C8 -0.3548 (6.1%) BOND C5 C7 Shown Composition: 00.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 61.6% BOND, 31.0% ANGLE, 0.3% OUT, 7.1% TOR
1606	Disperse Ring mode Largest Contribution: +0.4562 (3.1%) BOND C9 C8 Shown Composition: 0.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 33.5% BOND, 59.4% ANGLE, 0.2% OUT, 6.9% TOR
1603	Disperse Ring mode Largest Contribution: +0.4085 (3.0%) ANGLE C7 C23 C8 Shown Composition: 0.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 33.9% BOND, 59.8% ANGLE, 0.2% OUT, 6.2% TOR

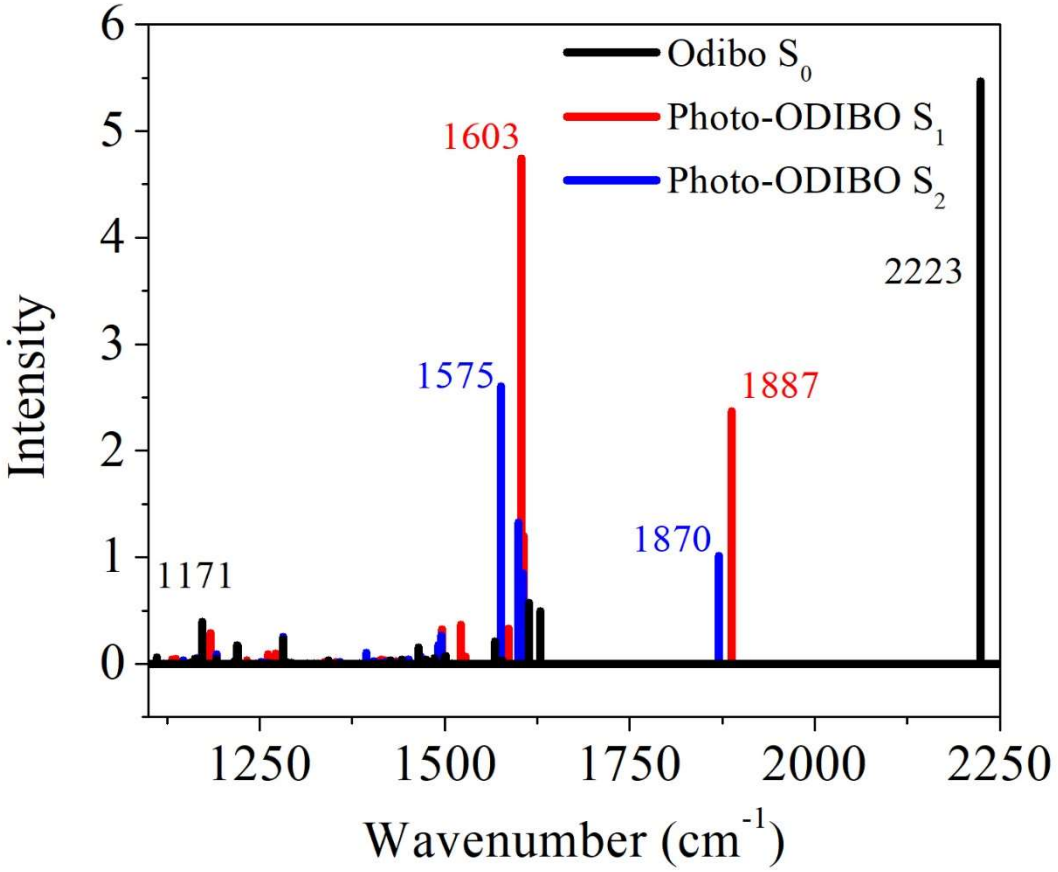
S_0Vibrational Mode (cm^{-1})	Decomposition
1893	-0.6975 (47.5%) BOND C23 O25 +0.2187 (14.9%) BOND C8 C23 +0.2144 (14.6%) BOND C7 C23 +0.1288 (8.8%) BOND C7 C8 -0.1058 (7.2%) BOND C5 C7 -0.1043 (7.1%) BOND C9 C8 Shown Composition: 100.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 100.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR
1642	-0.6845 (28.3%) BOND C7 C8 -0.4605 (19.0%) BOND C23 O25 +0.2332 (9.6%) BOND C9 C8 +0.2230 (9.2%) BOND C5 C7 Shown Composition: 100.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 84.6% BOND, 15.4% ANGLE, 0.0% OUT, 0.0% TOR
1604	-0.3985 (14.4%) BOND C3 C4 -0.3368 (12.1%) BOND C1 C6 +0.2884 (10.4%) BOND C5 C6 +0.2524 (9.1%) BOND C2 C3 Shown Composition: 100.0% BOND, 0.0% ANGLE, 0.0% OUT, 0.0% TOR Total Composition: 71.8% BOND, 27.0% ANGLE, 0.6% OUT, 0.6% TOR

ODIBO S_0 Geometry

ODIBO S_0 Geometry

C	6.5046390751	-0.5393423479	-1.0776176173
C	6.4396805901	-1.9339166356	-1.1625842905
C	5.1961635392	-2.5835787696	-1.0721948392
C	4.0246376943	-1.8634763309	-0.9020845154
C	4.0932188470	-0.4407002241	-0.8053803890
C	5.3322356098	0.1960743813	-0.8975953091
C	2.8327715237	0.1667365607	-0.5683324721
C	0.4562011223	-0.5586960704	0.0331990603
C	0.6736040358	-1.9365700517	0.3246937185
C	-0.4120296130	-2.7194491001	0.6981849826
C	-1.6909272397	-2.1628920482	0.7922568446
C	-1.9331476007	-0.8126641226	0.5062194181
C	-0.8342655612	-0.0281453585	0.1284902476
C	1.6380349261	0.1303457591	-0.3467085053
O	1.9306946571	-2.4879556770	0.3256306126
O	7.5148162483	-2.7516990972	-1.3328389281
H	7.4520268607	-0.0201749684	-1.1420523166
H	5.1796278451	-3.6658784324	-1.1462012489
H	5.3818171740	1.2764491211	-0.8225732108
H	-0.2446404268	-3.7656552130	0.9290998901
H	-2.5051773064	-2.8110298774	1.0907956925
C	-3.3323245077	-0.1766506313	0.5986582542
H	-0.9629647990	1.0239123104	-0.0990377995
C	8.8011057724	-2.1656052067	-1.4478231915
C	-3.3211433579	0.9386823093	1.6725324501
C	2.6806308435	-2.5720541748	-0.9159282221
C	-4.4178985524	-1.2031923875	0.9801374334
C	-3.7159766093	0.4374981562	-0.7703404287
H	2.0678880914	-2.1716852415	-1.7303041239
H	9.4955622825	-2.9968497277	-1.5848966524
H	2.8468751284	-3.6398165930	-1.0998335688
H	9.0721193147	-1.6082603549	-0.5410131166
H	8.8623104321	-1.4946307822	-2.3150218962
H	-4.3089580691	1.4106361556	1.7388880440
H	-2.5905766920	1.7185621710	1.4344787939
H	-3.0690770282	0.5286794909	2.6568419009
H	-5.3930770978	-0.7054844297	1.0188643313
H	-4.2302791694	-1.6473013457	1.9641301648
H	-4.4834485735	-2.0108499826	0.2425255478
H	-4.7090804647	0.8991191832	-0.7113706391
H	-3.7412210385	-0.3332186911	-1.5488587980
H	-3.0052446897	1.2096635002	-1.0815265304

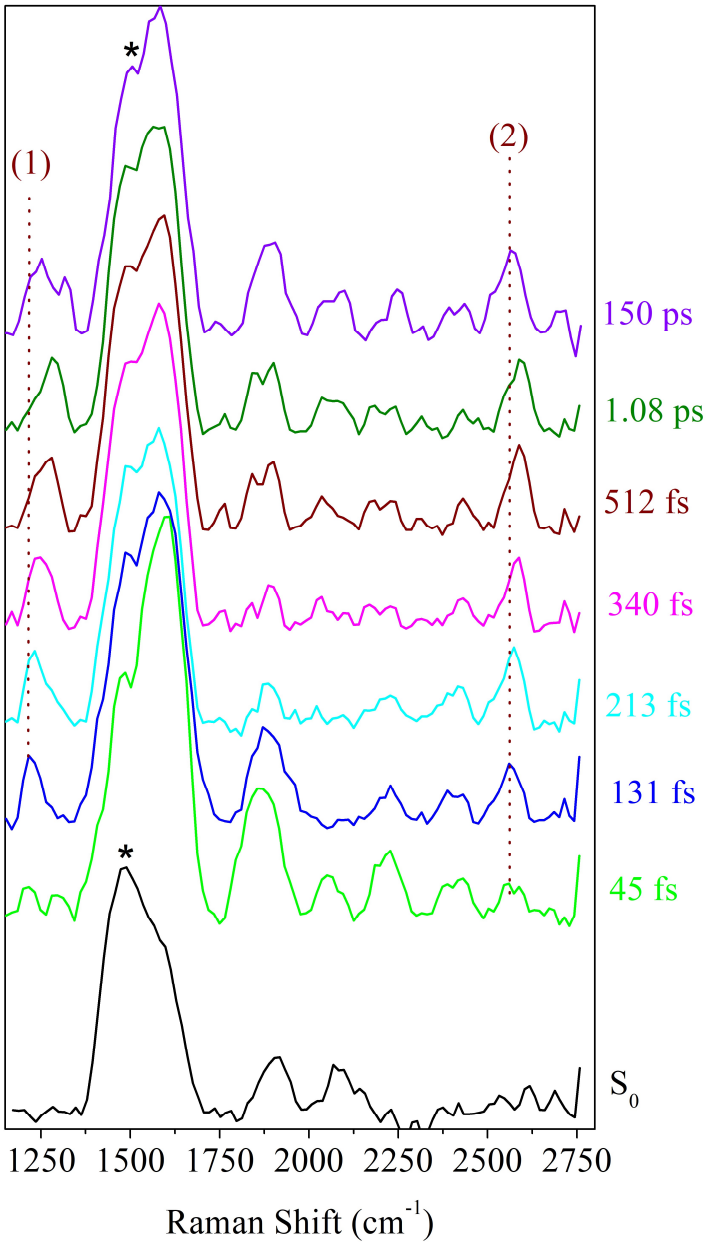
ODIBO and Photo-ODIBO Raman Spectra Compared



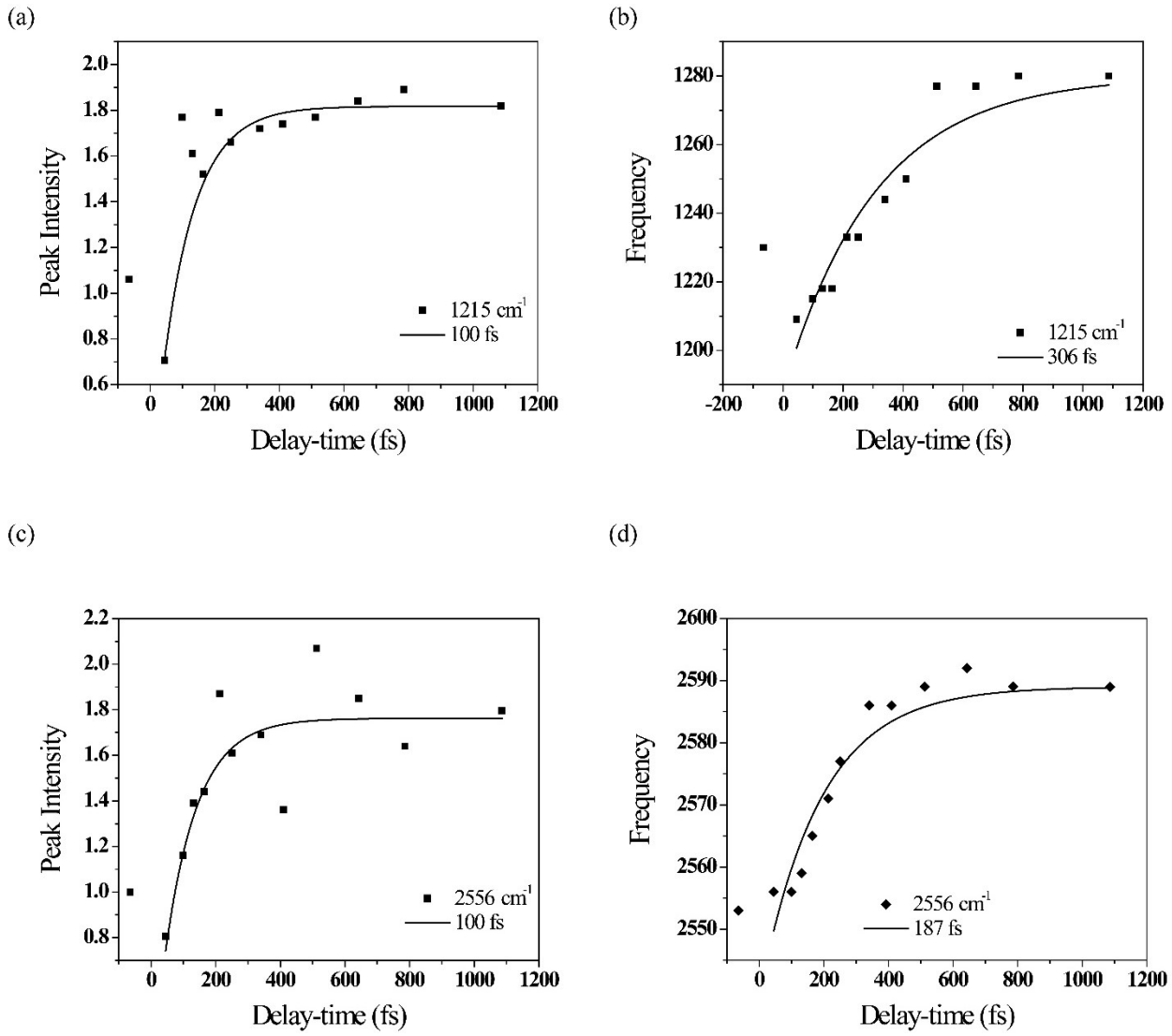
SI Figure 4: Comparison of Photo-ODIBO (S_2 and S_1) Raman spectra and ODIBO S_0

3. Additional Photo-ODIBO FSRS Dynamics

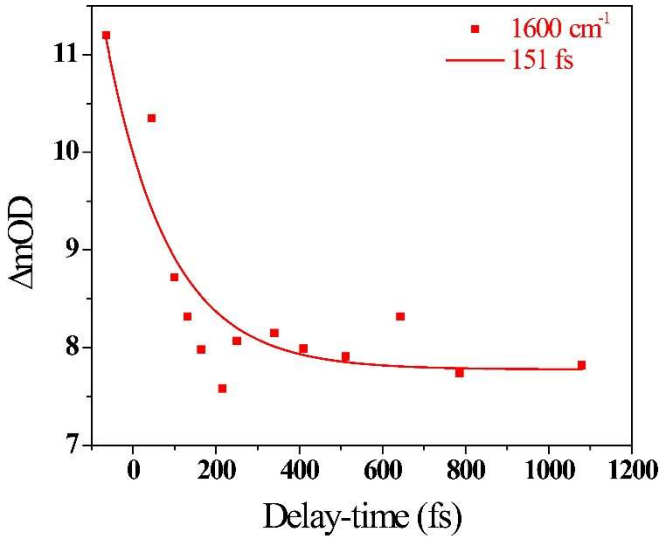
Additional dynamics for shifting and splitting Photo-ODIBO FSRS peaks are provided here. The position and intensity for the peak maxima obtained from the FSRS spectra were plotted in each case.



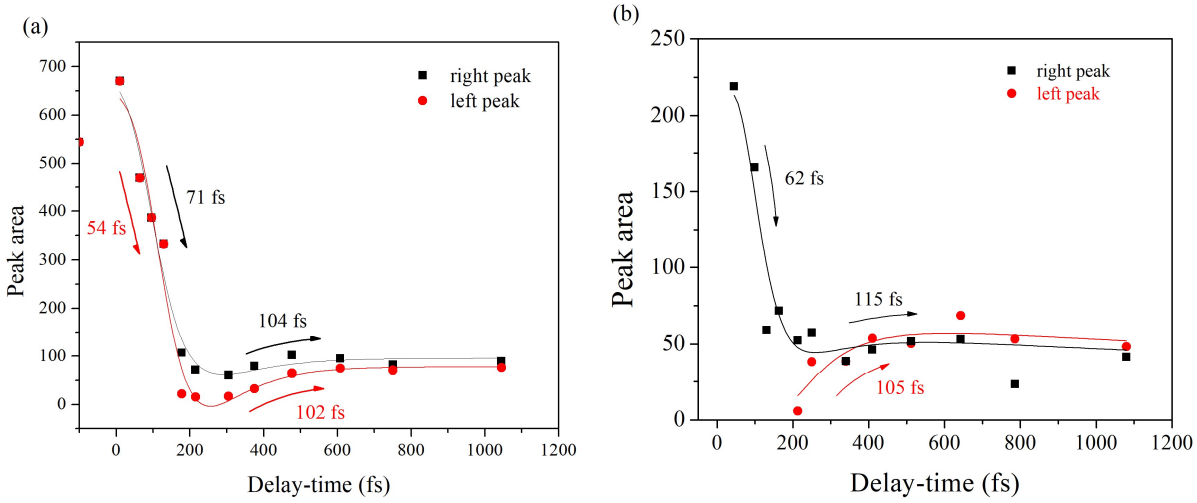
SI Figure 5: Photo-ODIBO FSRS spectra at various pump-probe delays after 321 nm excitation and ground state spectrum (black). The peaks in the excited state spectrum are labeled **(1)** - 1215 cm^{-1} and **(2)** – 2556 cm^{-1}. The black star denotes a methanolic 1483 cm^{-1} peak.



SI Figure 6**:** (a), (b) Intensity and blue-shift dynamics for the 1215 cm^{-1} peak. (c) Intensity as a function of time for the 2553 peak (100 fs exponential rise). (d) Peak shift kinetics for the 2553 mode with a single exponential fit (187 fs time constant)



SI Figure 7: Kinetics for the 1600 cm^{-1} peak assigned to a combination of overlapping $^{S2}\upsilon_{C=C}$[PO], $^{S2}\upsilon_{ring}$[PO] modes at 1575, 1605, and 1599 cm^{-1}. A single exponential fit with a 151 fs lifetime was used to describe the dynamics.



SI Figure 8: (a) Peak area plotted as a function of pump-probe delay for the ~1870 cm^{-1} peaks of Photo-ODIBO, including decay and rise times. (b) Peak area plotted as a function of pump-probe delay for the 2100-2300 cm^{-1} peaks of Photo-ODIBO. The right peak at ~2230 cm^{-1} is described by a decay and rise, whereas the left peak at ~2165 cm^{-1} shows a delayed rise. In both cases an additional ~4 ps decay is included in the fit to account for the decrease in signal at longer delays.

The peak area analysis reproduces the general trends observed in the peak intensity analysis presented in Figures 6(b) and 7(b) of the main manuscript and the time constants are similar.

4. Two-component Decay Model

$$y = \boldsymbol{y_0} + \sum_i \boldsymbol{A_i} * e^{\frac{\left(G/_{2\cdot\sqrt{ln}}\right)^2 - 4*\boldsymbol{dec_i}*(t-\boldsymbol{t_0})}{4*\boldsymbol{dec_i}^2}} \cdot \left(1 - erf\frac{\left(G/_{2\cdot\sqrt{ln}}\right)^2 - 2\cdot\boldsymbol{dec_i}\cdot(t-\boldsymbol{t_0})}{2\cdot\sqrt{ln2}\cdot\boldsymbol{dec_i}}\right) \quad (1)$$

Where,

y_0 is the intensity offset

A_i is the exponential amplitude

dec_i is the time constant for the decay

G is the IRF FWHM

The sequential decay model (Equation 1) is used to extract time constants for the peak intensity dynamics as a function of time.