Supporting information for

# Hydrogen Bonding Tunes the Early Stage of Hydrogen-Atom Abstracting Reaction

*Yang Yang, Lei Liu, Junsheng Chen, and Keli Han**

State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Corresponding Author(s)' e-mail address: klhan@dicp.ac.cn

Table of contents Page

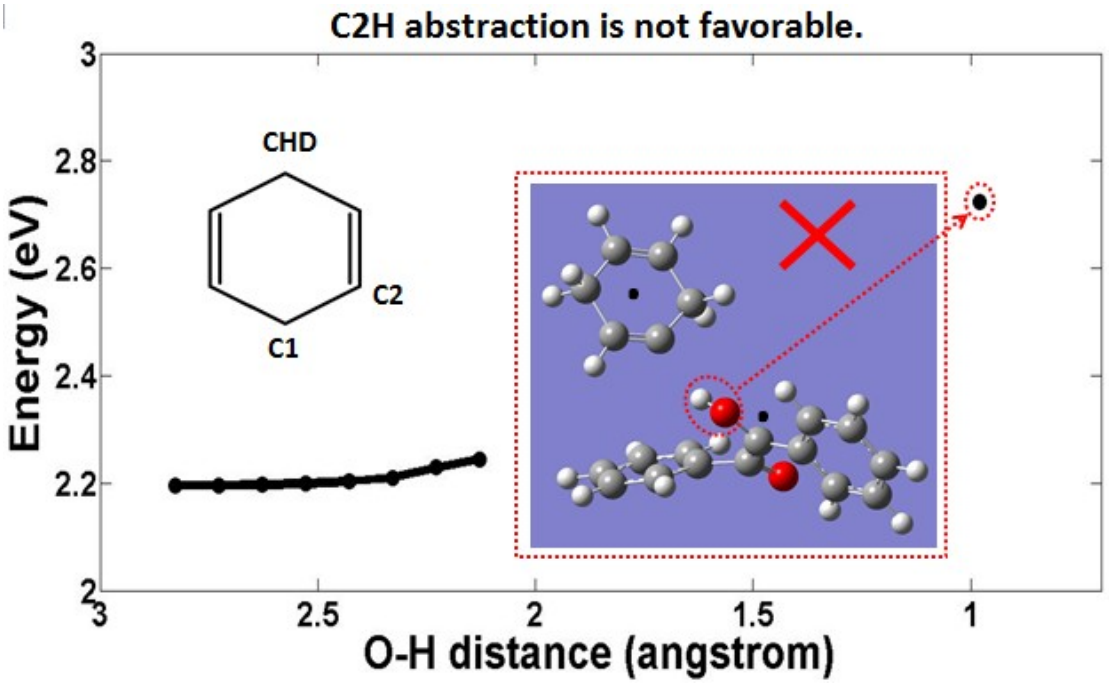



Figure S1. The excited-state energy variation of the dimer with O-H distance on the carbonyl of $T_1$ benzil

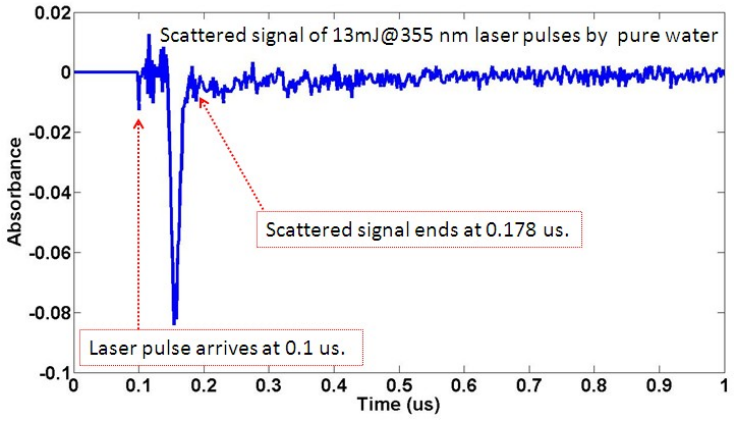
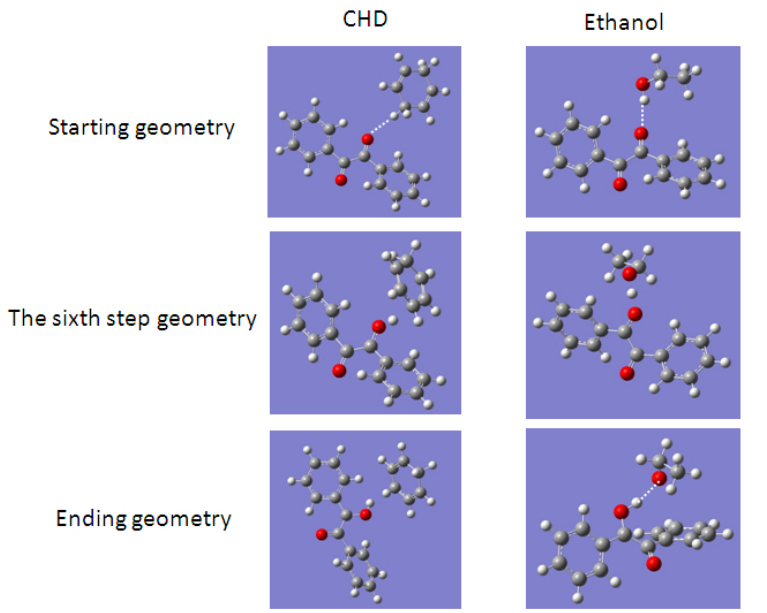



Figure S2. The apparatus response of our transient absorption spectroscopy

As can be seen clearly from the above figure, the laser pulse irradiates the sample at 0.1 us and the apparatus response ends at 0.178 us. The apparatus response ends thoroughly within 0.078 us (within 100 ns). Since the "climb-up" and "fast decay" of fig 2a are on the order of microseconds, much longer than 100 ns, we can make sure that they are the signal caused by the triple benzil rather than the apparatus response.




Different stages of hydrogen atom abstracting stage

**The corresponding coordinates of hydrogen atom abstracting are also shown as follows:**

**CHD, Starting geometry C-H 1.10 O-H 2.68**

| | | | |
|---|---|---|---|
| C | -0.64680600 | 4.70051800 | 0.09520600 |
| C | 0.39760100 | 4.31773700 | 0.94267000 |
| C | 0.95390400 | 3.04081800 | 0.84642800 |
| C | 0.47258400 | 2.13721300 | -0.11923500 |
| C | -0.60023500 | 2.51698400 | -0.95181400 |
| C | -1.14334800 | 3.79546100 | -0.85182700 |
| C | 1.02308300 | 0.76505800 | -0.26748900 |
| O | 0.29025800 | -0.15190500 | -0.71740700 |
| C | 2.44610100 | 0.48766900 | 0.05548400 |
| O | 3.21652200 | 1.43747600 | 0.34331000 |
| C | 2.98028400 | -0.89721800 | -0.01600600 |

| | | | |
|---|---|---|---|
| C | 4.35620800 | -1.06478000 | -0.27575600 |
| C | 4.90102700 | -2.34368800 | -0.35864000 |
| C | 4.09193700 | -3.46930300 | -0.15659900 |
| C | 2.73313200 | -3.30676500 | 0.13068100 |
| C | 2.17534800 | -2.02918400 | 0.20945300 |
| H | -1.07682200 | 5.69421000 | 0.17615500 |
| H | 0.77193000 | 5.00719700 | 1.69309100 |
| H | 1.74355500 | 2.74698900 | 1.52668400 |
| H | -0.97825500 | 1.81492000 | -1.68681700 |
| H | -1.95077400 | 4.08912700 | -1.51572900 |
| H | 4.97745000 | -0.19061700 | -0.43696900 |
| H | 5.95576900 | -2.46415000 | -0.58658900 |
| H | 4.52041600 | -4.46522900 | -0.21527200 |
| H | 2.10578000 | -4.17439400 | 0.31018400 |
| H | 1.12782000 | -1.91615700 | 0.45914600 |
| C | -4.24425900 | -0.16988300 | -0.15573800 |
| C | -3.15455300 | -0.76429300 | 0.69937900 |
| C | -3.35733500 | -2.23330200 | 0.96932200 |
| C | -4.39592100 | -2.93668000 | 0.49954300 |
| C | -5.48658400 | -2.34141300 | -0.35449500 |
| C | -5.28337700 | -0.87224900 | -0.62563000 |
| H | -4.16118100 | 0.88980900 | -0.39120300 |
| H | -2.17437500 | -0.60274900 | 0.22265700 |
| H | -3.08560200 | -0.21512300 | 1.65226300 |
| H | -2.60562700 | -2.72870700 | 1.58169600 |
| H | -4.47856400 | -3.99664700 | 0.73409000 |
| H | -6.46559400 | -2.50099800 | 0.12510300 |

| | | | |
|---|---|---|---|
| H | -5.55810100 | -2.89097100 | -1.30672200 |
| H | -6.03481900 | -0.37726700 | -1.23861400 |

CHD, The sixth step geometry C-H 1.61 O-H 1.03

| | | | |
|---|---|---|---|
| C | 4.36606800 | -2.21915900 | 0.14101400 |
| C | 3.39051600 | -2.78497000 | 0.97096500 |
| C | 2.05925400 | -2.38419500 | 0.87205500 |
| C | 1.67582900 | -1.39184200 | -0.05663100 |
| C | 2.67050100 | -0.82921200 | -0.88725700 |
| C | 3.99850600 | -1.24272200 | -0.79146800 |
| C | 0.28802800 | -0.93515400 | -0.16718800 |
| O | 0.02694400 | 0.33804000 | -0.50464400 |
| C | -0.84784100 | -1.83107200 | -0.05976600 |
| O | -0.67336700 | -3.07390700 | -0.00426500 |
| C | -2.25001600 | -1.29416500 | -0.05552400 |
| C | -3.24779800 | -2.06676300 | -0.67627900 |
| C | -4.58168100 | -1.65775500 | -0.65790000 |
| C | -4.94350500 | -0.47923000 | 0.00449500 |
| C | -3.96170500 | 0.28716200 | 0.64105600 |
| C | -2.62277300 | -0.10967400 | 0.60403200 |
| H | 5.40118000 | -2.53777600 | 0.21883200 |
| H | 3.66932700 | -3.53961100 | 1.70048900 |
| H | 1.31187900 | -2.82525100 | 1.52005300 |
| H | 2.39315400 | -0.09037400 | -1.63251600 |
| H | 4.74497600 | -0.80704800 | -1.44889900 |
| H | -2.96372300 | -2.98780600 | -1.17507500 |
| H | -5.33795300 | -2.25805700 | -1.15531600 |

| | | | |
|---|---|---|---|
| H | -5.98219400 | -0.16250200 | 0.02676800 |
| H | -4.23777500 | 1.19633300 | 1.16733800 |
| H | -1.87190600 | 0.49518000 | 1.09833200 |
| C | 1.58438500 | 3.03992300 | -0.97614400 |
| C | 1.62132700 | 2.28977700 | 0.24346000 |
| C | 0.83376300 | 2.73227300 | 1.35580600 |
| C | -0.04211800 | 3.77276600 | 1.23548600 |
| C | -0.21172700 | 4.52653100 | -0.05024200 |
| C | 0.72038200 | 4.08514300 | -1.13951500 |
| H | 2.24659800 | 2.75537600 | -1.78969800 |
| H | 0.73823900 | 1.03025800 | -0.22432900 |
| H | 2.43541300 | 1.59006900 | 0.41620800 |
| H | 0.92779600 | 2.21116100 | 2.30489300 |
| H | -0.64080800 | 4.08495300 | 2.08683500 |
| H | -0.09712500 | 5.61002900 | 0.12911200 |
| H | -1.25885300 | 4.44275800 | -0.39713600 |
| H | 0.69679300 | 4.63328200 | -2.07735800 |

CHD, Ending geometry C-H 2.51 O-H 0.97

| | | | |
|---|---|---|---|
| C | -2.38967800 | 4.04704700 | 0.12033000 |
| C | -1.08537400 | 4.27402500 | 0.57769100 |
| C | -0.12250300 | 3.27131000 | 0.49871100 |
| C | -0.44760800 | 2.00314000 | -0.03923100 |
| C | -1.77017500 | 1.78818700 | -0.49431900 |
| C | -2.72556400 | 2.79967000 | -0.41668800 |
| C | 0.52882100 | 0.92411600 | -0.09947900 |
| O | 0.10376400 | -0.36105200 | -0.12843800 |

| | | | |
|---|---|---|---|
| C | 1.96201100 | 1.11287700 | -0.23614400 |
| O | 2.42779600 | 2.24272400 | -0.51353200 |
| C | 2.90111300 | -0.04836300 | -0.08717700 |
| C | 4.04872600 | -0.07157600 | -0.89907500 |
| C | 4.99310300 | -1.09007300 | -0.76674000 |
| C | 4.81602100 | -2.08795200 | 0.19838100 |
| C | 3.68760900 | -2.06242300 | 1.02451500 |
| C | 2.73005600 | -1.05618100 | 0.87782200 |
| H | -3.13512400 | 4.83407700 | 0.18099300 |
| H | -0.81919900 | 5.23702900 | 1.00309900 |
| H | 0.88065300 | 3.45481700 | 0.86069200 |
| H | -2.04844300 | 0.84050400 | -0.94503200 |
| H | -3.73056200 | 2.61585700 | -0.78407300 |
| H | 4.18822500 | 0.71343300 | -1.63537500 |
| H | 5.86681600 | -1.10409500 | -1.41167200 |
| H | 5.55358300 | -2.87764900 | 0.30774400 |
| H | 3.55123600 | -2.82714400 | 1.78353000 |
| H | 1.85937400 | -1.04814100 | 1.52335000 |
| C | -3.71368800 | -1.33755200 | 0.67435300 |
| C | -2.55006500 | -1.90719600 | 1.26509600 |
| C | -1.95860900 | -3.06173500 | 0.67730700 |
| C | -2.47472100 | -3.62749500 | -0.45811100 |
| C | -3.68608100 | -3.06788100 | -1.14903000 |
| C | -4.26845700 | -1.86560000 | -0.46118000 |
| H | -4.16866400 | -0.46658800 | 1.13934800 |
| H | -0.81380200 | -0.45511400 | 0.18530500 |
| H | -2.14426600 | -1.49193300 | 2.18251100 |

| | | | |
|---|---|---|---|
| H | -1.07996300 | -3.50016300 | 1.14405800 |
| H | -2.00784300 | -4.50829400 | -0.89102600 |
| H | -4.45715000 | -3.85306500 | -1.25537200 |
| H | -3.43985000 | -2.81930800 | -2.19855300 |
| H | -5.15713000 | -1.41565500 | -0.89594500 |

**Oxygen atom on ethanol: O1 Oxygen atom on benzil: O2**

**Ethanol, Starting geometry O1-H 0.97 O2-H 1.99**

| | | | |
|---|---|---|---|
| C | -4.90677900 | 0.37024600 | -0.09194800 |
| C | -3.84033400 | 1.18074800 | 0.29838500 |
| C | -2.55077200 | 0.66116500 | 0.37024100 |
| C | -2.32106300 | -0.68159600 | 0.03060400 |
| C | -3.40287700 | -1.50476800 | -0.33070900 |
| C | -4.68391200 | -0.97301300 | -0.40585000 |
| C | -0.96467400 | -1.28554200 | 0.09289300 |
| O | -0.85530800 | -2.49621500 | 0.38818000 |
| C | 0.22989400 | -0.47819100 | -0.24890600 |
| O | 0.08804300 | 0.67760900 | -0.70326200 |
| C | 1.58447400 | -1.07354500 | -0.12052200 |
| C | 2.60232800 | -0.59403500 | -0.96398400 |
| C | 3.88045700 | -1.13313800 | -0.88922500 |
| C | 4.16893600 | -2.13237700 | 0.04415400 |
| C | 3.17042600 | -2.58936300 | 0.90368600 |
| C | 1.88362700 | -2.06084900 | 0.83153100 |
| H | -5.90875100 | 0.78023800 | -0.14336200 |
| H | -4.01266300 | 2.21730200 | 0.56318300 |

| | | | |
|---|---|---|---|
| H | -1.73725600 | 1.29086100 | 0.70157000 |
| H | -3.22404600 | -2.54350200 | -0.57773800 |
| H | -5.50959400 | -1.60419800 | -0.71317000 |
| H | 2.37247400 | 0.17600600 | -1.68935500 |
| H | 4.65222500 | -0.77952800 | -1.56310400 |
| H | 5.16896100 | -2.54593400 | 0.10531700 |
| H | 3.39481400 | -3.34669400 | 1.64558900 |
| H | 1.12750900 | -2.40173900 | 1.52509600 |
| C | 2.73620500 | 3.90402800 | -0.17415600 |
| C | 1.53133400 | 3.86756400 | 0.75740100 |
| O | 0.31710800 | 3.50997600 | 0.08514000 |
| H | 3.63000700 | 4.21809700 | 0.37383300 |
| H | 2.57104900 | 4.60760800 | -0.99456000 |
| H | 2.93280600 | 2.91609400 | -0.60079300 |
| H | 1.35110600 | 4.85751000 | 1.18297100 |
| H | 1.71590300 | 3.17965200 | 1.59186200 |
| H | 0.37309000 | 2.58327200 | -0.18938100 |

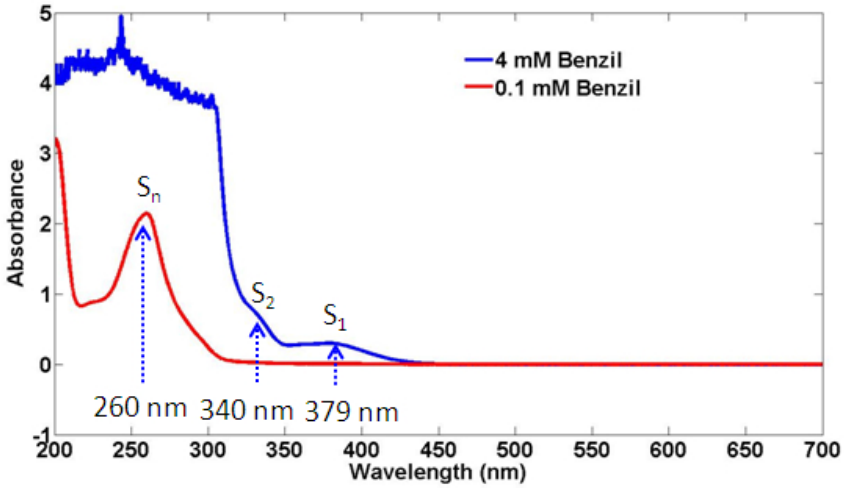
**Ethanol, The ninth step geometry O1-H 1.13 O2-H 1.19**

| | | | |
|---|---|---|---|
| C | 5.00669600 | 0.51212000 | -0.03021000 |
| C | 3.95133700 | 1.29970800 | -0.49159100 |
| C | 2.65409500 | 0.79455600 | -0.51006300 |
| C | 2.40315000 | -0.51159600 | -0.06214500 |
| C | 3.47416000 | -1.30969400 | 0.37348900 |
| C | 4.76428400 | -0.79315400 | 0.40513500 |
| C | 1.03958700 | -1.12403500 | -0.10378900 |
| O | 0.94054900 | -2.32399400 | -0.42737500 |

| | | | |
|---|---|---|---|
| C | -0.13074600 | -0.32465900 | 0.26312700 |
| O | 0.09437600 | 0.84221100 | 0.77622400 |
| C | -1.49357200 | -0.86703000 | 0.15297500 |
| C | -2.48802000 | -0.41903500 | 1.04147000 |
| C | -3.78139100 | -0.92551200 | 0.96751400 |
| C | -4.11259100 | -1.87505600 | -0.00126800 |
| C | -3.13761200 | -2.31531400 | -0.89622800 |
| C | -1.83824200 | -1.81937300 | -0.82445100 |
| H | 6.01460800 | 0.91065800 | -0.01606700 |
| H | 4.13894700 | 2.30647400 | -0.84638200 |
| H | 1.84540400 | 1.40503400 | -0.88689700 |
| H | 3.28036500 | -2.32350800 | 0.70108200 |
| H | 5.58180800 | -1.40673300 | 0.76557900 |
| H | -2.24307800 | 0.31080300 | 1.80098800 |
| H | -4.52945300 | -0.58635700 | 1.67485700 |
| H | -5.12213800 | -2.26534600 | -0.05912200 |
| H | -3.39022400 | -3.03705200 | -1.66443800 |
| H | -1.10075700 | -2.15220300 | -1.54051900 |
| C | -2.96002100 | 2.98363800 | -0.92733000 |
| C | -1.56153100 | 3.26732200 | -0.37149100 |
| O | -1.33664400 | 2.67448100 | 0.87968400 |
| H | -3.09597100 | 3.51730400 | -1.87178800 |
| H | -3.72804700 | 3.31548300 | -0.22523900 |
| H | -3.08618200 | 1.91420300 | -1.10767600 |
| H | -1.46510900 | 4.35413700 | -0.20860900 |
| H | -0.78221400 | 2.97719600 | -1.08566600 |
| H | -0.64169700 | 1.78101800 | 0.83076800 |

| Ethanol, Ending geometry | O1-H 1.81 | O2-H 0.98 | |
|---|---|---|---|
| C | 4.06767500 | -1.68282700 | -0.66199300 |
| C | 3.05170000 | -1.60362100 | -1.61452800 |
| C | 1.74782800 | -1.30570600 | -1.22402600 |
| C | 1.44310300 | -1.10024100 | 0.12917700 |
| C | 2.46748900 | -1.20090600 | 1.08145500 |
| C | 3.77301300 | -1.47747100 | 0.68741500 |
| C | 0.03362800 | -0.89512900 | 0.60485800 |
| O | -0.33766100 | -1.44064400 | 1.66051100 |
| C | -0.86894800 | -0.05996800 | -0.17345300 |
| O | -0.37793800 | 0.84458100 | -1.04261000 |
| C | -2.31771600 | -0.11075200 | -0.10057300 |
| C | -3.07673200 | 0.92761800 | -0.68837100 |
| C | -4.46510100 | 0.89665000 | -0.66436400 |
| C | -5.13707700 | -0.16957200 | -0.06233600 |
| C | -4.40167800 | -1.20833600 | 0.51426500 |
| C | -3.01291600 | -1.18568900 | 0.49972200 |
| H | 5.08309500 | -1.90715600 | -0.96845300 |
| H | 3.27329200 | -1.77668200 | -2.66146400 |
| H | 0.96512700 | -1.25328200 | -1.97163400 |
| H | 2.22889900 | -1.05955800 | 2.12884200 |
| H | 4.55992700 | -1.53889800 | 1.43059300 |
| H | -2.56256600 | 1.75786600 | -1.15347600 |
| H | -5.02669200 | 1.70750100 | -1.11450100 |
| H | -6.22065700 | -0.19233400 | -0.04467000 |
| H | -4.91564700 | -2.04410500 | 0.97555300 |

| | | | |
|---|---|---|---|
| H | -2.45762500 | -1.99623300 | 0.94783000 |
| C | 2.09700900 | 3.14775600 | 1.48274000 |
| C | 1.91397600 | 3.34948000 | -0.05710800 |
| O | 2.03980600 | 2.10999400 | -0.63155400 |
| H | 2.00283200 | 4.13250800 | 1.94411300 |
| H | 3.08244700 | 2.73551800 | 1.69672300 |
| H | 1.32483100 | 2.48575700 | 1.87334800 |
| H | 2.70665200 | 4.02314100 | -0.40573200 |
| H | 0.91913100 | 3.77887200 | -0.23071000 |
| H | 0.55177100 | 1.10792500 | -0.85442000 |




| Electronic state | Abs. wavelength（nm） | Oscillator strength | Contribution |
|---|---|---|---|
| S1 | 394 | 0.0012 | H→L |
| S2 | 341 | 0.0092 | H→L+1, H-5→L |
| S3 | 292 | 0.0501 | H-1→L, H-3→L |
| S4 | 290 | 0.0024 | H-2→L |
| S5 | 286 | 0.2242 | H-4→L,H-1→L |
| S6 | 275 | 0.0151 | H-5→L,H-4→L |
| S7 | 265 | 0.0082 | H-4→L+1,H-1→L+1 |
| S8 | 264 | 0.1017 | H-2→L+1 |
| S9 | 251 | 0.2696 | H-5→L,H-4→L+1 |
| S10 | 250 | 0.1411 | H-3→L+1,H-1→L+1 |
| S11 | 238 | 0.0837 | H-5→L |
| S12 | 230 | 0.0000 | H→L+2 |

As can be seen clearly, benzil in acetonitrile has three main absorption bands peaking at around 379 nm, 340 nm and 260 nm, which can be attributed to the transitions from $S_0$ to $S_1$, $S_2$ and $S_n$, respectively. These results suggest the single photon excitation of 355 nm laser pulse will only promote the transition of benzil from $S_0$ to $S_1$.