PCCP

ARTICLE TYPE

Theoretical and experimental study on the O(^{3}P) + 2,5-dimethylfuran reaction in the gas phase

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Supplementary Information

1 Absolute Photoionization Spectra

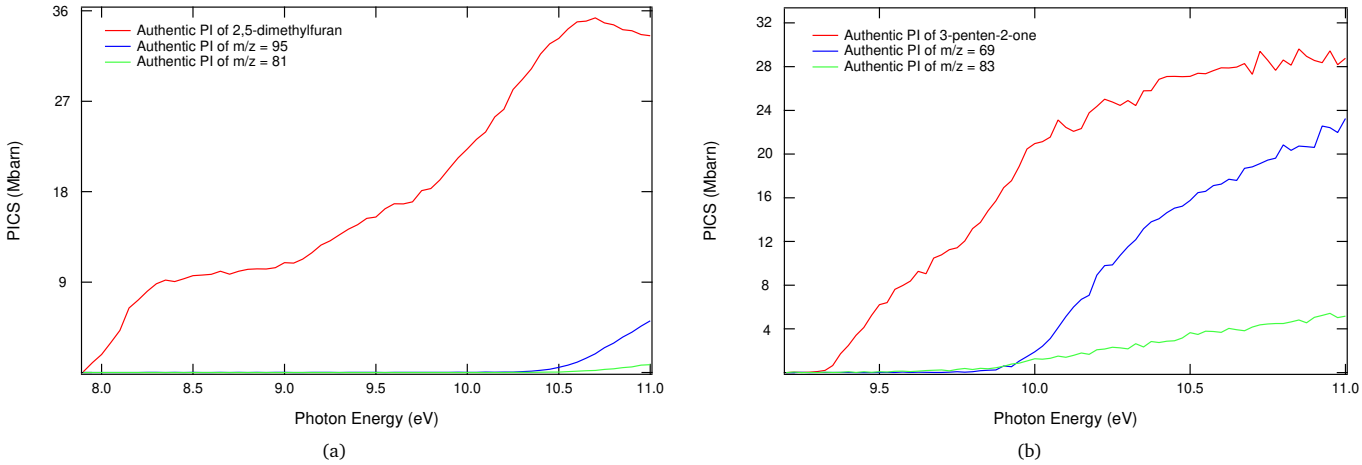

Fig. 1 (a) Absolute photoinization spectrum of 2,5-dimethylfuran and its fragments; (b) Absolute photoinization spectrum of 3-penten-2-one and its fragments.

2 MultiWell Simulations

Figures 2(a) and 2(b) illustrate the outcomes from the simulations performed at 100 Torr and 0 Torr. At 100 Torr the system shows a high-pressure limit behavior with all the intermediates populations thermalized, thus stuck in the deep wells of the singlet PES without any chance to overcome the high energy barriers. On the other hand, at 0 Torr the system is characterized by a fully non-thermal distribution of the energized intermediates causing every unimolecular decomposition pathway on the singlet PES to open up.

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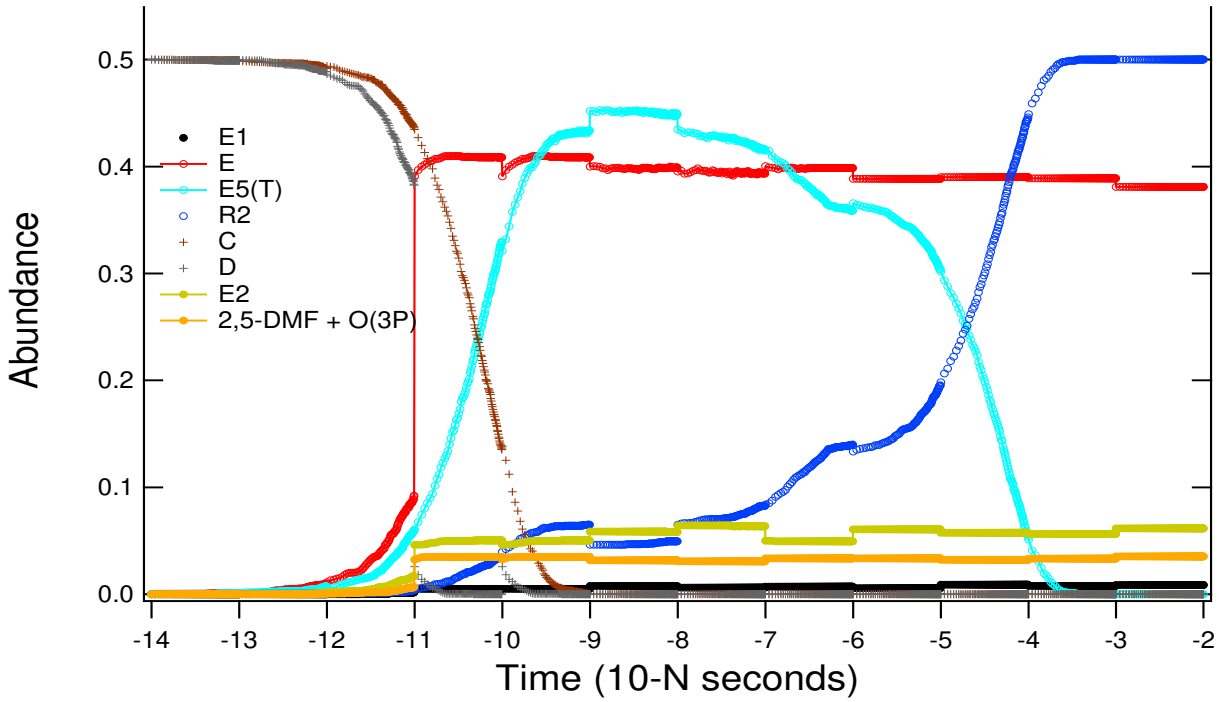
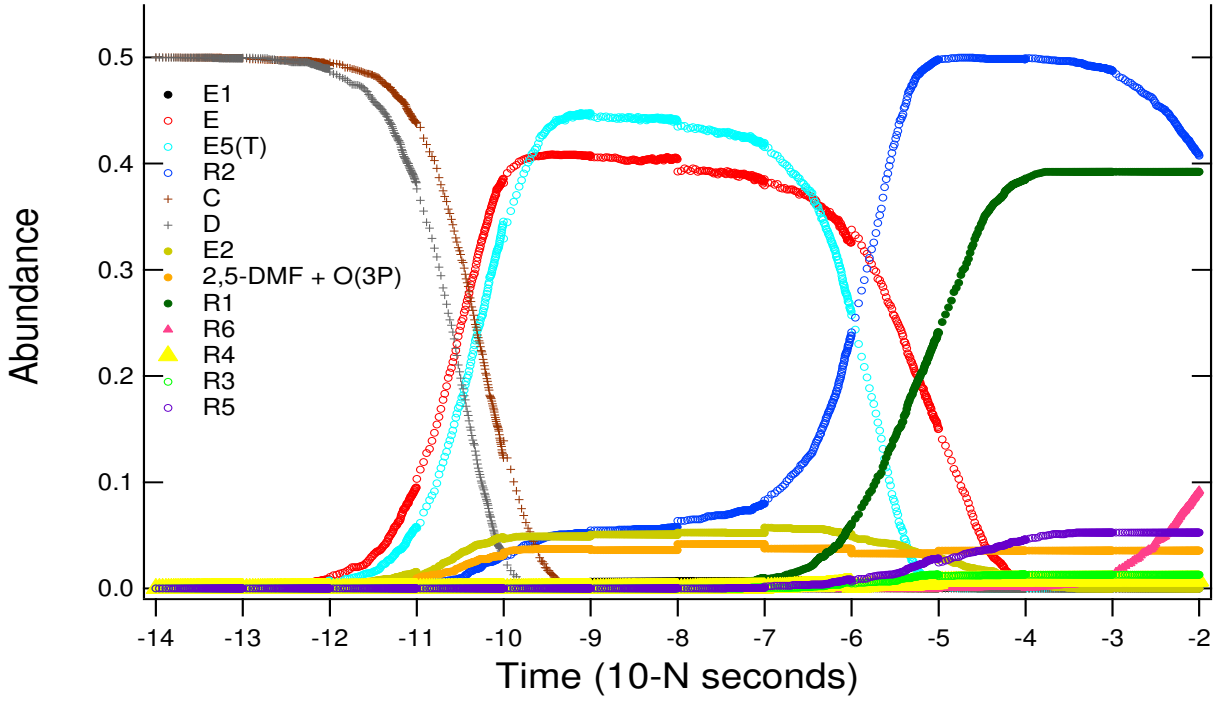


(a)



(b)

Fig. 2 (a) MultiWell kinetic modelling of the 2,5-DMF + O(3P) system in the $10^{-16} - 10^{-2}$ seconds time range at 550 K and 150 Torr; (b) MultiWell kinetic modelling of the 2,5-DMF + O(3P) system in the $10^{-16} - 10^{-2}$ seconds time range at 550 K and 0 Torr. The observed discontinuities derive from numerical artifacts of the integration, not significantly affecting the final outcome, due to the use of different length of the simulations necessary for reporting the time-course of the different involved intermediates and products along the whole time range of interest.

3 Vibrational Energies

Figure 3 illustrates the mean vibrational energies time evolution of every intermediates in the global potential energy surface . Interestingly, despite the system has been found to be under non-thermal conditions, the collisional model manages to reproduce the deactivation event regarding the high-energized species deriving from the reaction between 2,5-dimethylfuran and O(^{3}P). After 20 microseconds the system is showed to be almost entirely thermalized. This result backs up our assumption that the products arising from our experiment are formed in less than 1 milliseconds (which is the time resolution of the kinetic traces from MPIMS experiments) and what we are able to retrieve is the tail of non-thermal reactions.

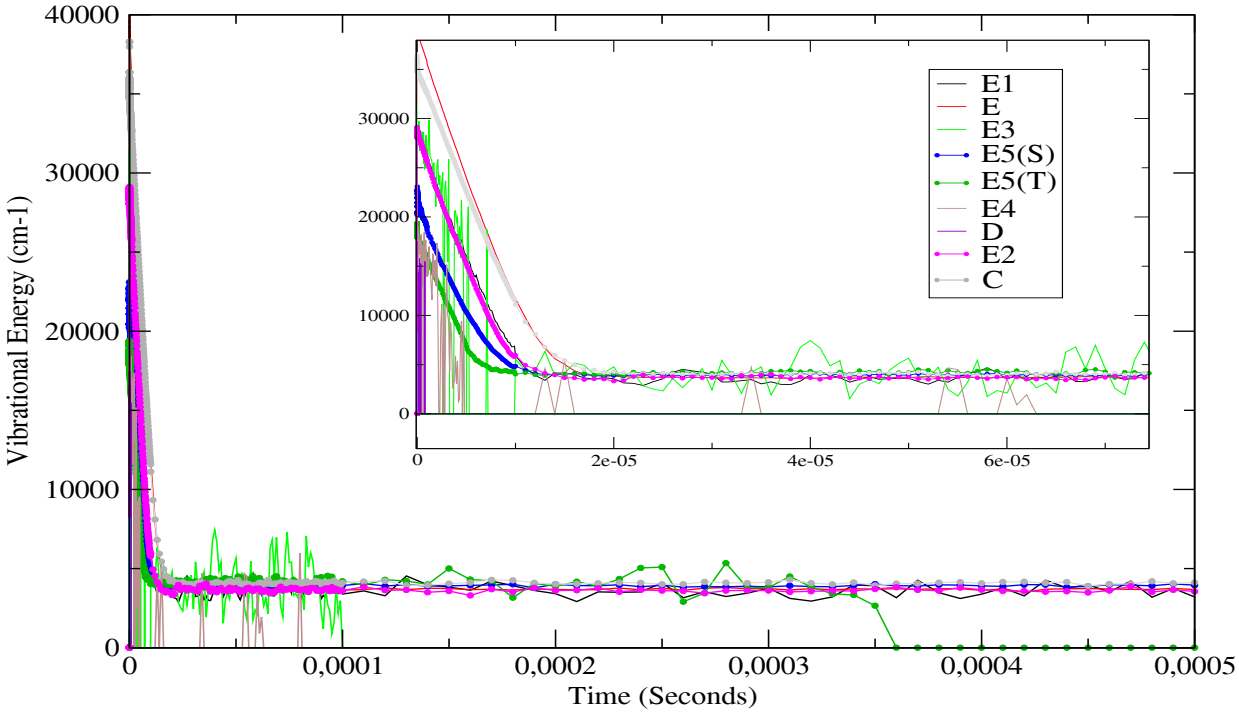


Fig. 3 Mean vibrational energies in cm^{-1} of the intermediates and the adducts from the potential energy surface over the time evolution (*seconds*). Highlighted is a close-up of the mean vibrational energies time changing between 0 and 60 μs.

4 Electronic Structures

Both the intermediates and the transition states electronic structures have been optimized at the CBS-QB3 composite method by using the Gaussian09 computational software.[1] The transition states are reported along with the corresponding computed vibrational frequencies. MECP electronic structures have been optimized by using the wB97XD/6-311+G* level of theory[2] by employing the GAMESS computational software.[3] We followed the reaction coordinate of the O(^{3}P) addition to 2,5-DMF to form adduct C and D through the costrained optimization procedure[4,5] and the Hessian matrix was computed at each step to revaluate the to-the-path orthogonal vibrational frequencies for the the loose transition state allocation. Cartesian coordinates are presented below.

4.1 Intermediates

```
ADDUCT C
C -0.89953400 -0.54394200 -0.34466900
C -0.79493600 0.95723800 -0.44083800
C 0.71229500 1.13090200 -0.37530300
C 1.25759300 -0.05167100 -0.04002600
O 0.33652900 -1.06394400 0.04050200
H -1.26910200 1.38780500 -1.33467700
H 1.21845600 2.07660200 -0.47320900
C -2.08640200 -1.32664300 0.07231100
H -1.93443700 -2.39293500 -0.11331800
H -2.29857300 -1.19806600 1.14395100
H -2.97043200 -0.99955100 -0.48023400
C 2.66697500 -0.45201100 0.20320400
H 2.97750700 -1.21881400 -0.51236900
H 3.33180500 0.40713300 0.11678700
H 2.76875800 -0.87872500 1.20560800
O -1.20652000 1.63060800 0.70942100
ADDUC D
C -1.01027600 -0.05315100 0.13483400
C -0.50950700 1.36460100 -0.11942200
C 0.86954700 1.30918000 -0.20088700
C 1.29213000 -0.00077200 -0.01594500
O 0.24304100 -0.84094000 0.18452100
H -1.17451200 2.20981700 -0.18322000
H 1.53040700 2.14223500 -0.39434600
C -1.86765900 -0.65504500 -1.01518000
H -1.28372600 -0.62172400 -1.93490100
H -2.11784100 -1.68971700 -0.77676500
H -2.78072600 -0.07116300 -1.12819800
C 2.64737100 -0.60126000 0.00944700
H 2.74872900 -1.37745000 -0.75769500
H 3.40952200 0.16015900 -0.16202500
H 2.84120500 -1.07986600 0.97606300
O -1.70587800 -0.14076200 1.26598000
INTERMEDIATE E
C -0.82420000 -0.62866700 -0.44893500
C 1.27280800 0.11229800 0.00349700
C 0.51894800 1.22475600 0.17165200
C -0.86692200 0.86740200 -0.07926000
H 0.87439600 2.20122900 0.45958700
H -1.10496300 -0.74941900 -1.49915600
O 0.57996200 -0.99517700 -0.34782600
O -1.88413500 1.52819600 -0.02333700
C 2.73906700 -0.08914500 0.14336100
```

H 2.94047500 -0.86254600 0.88998900
H 3.23509200 0.83451500 0.43898600
H 3.15965900 -0.43637300 -0.80478900
C -1.67296800 -1.50533000 0.45206300
H -1.33696000 -1.42837700 1.48873200
H -1.62701800 -2.55116900 0.14307400
H -2.70769300 -1.15989500 0.39861300
INTERMEDIATE E1
C 0.98960800 0.18482400 0.00874400
C -1.25868700 0.04237000 -0.08358600
C -0.84846900 -1.19528700 -0.41090500
C 0.62487500 -1.19858000 -0.34842600
H -1.48537100 -2.03581000 -0.63638200
H 1.25950500 -1.88519100 -0.89511400
O -0.22071700 0.92414000 0.12355500
O 1.14823100 -0.81240700 0.98406500
C -2.61667000 0.61677200 0.09948200
H -2.76649900 0.91904900 1.14028400
H -3.38151600 -0.11315700 -0.16680800
H -2.74073500 1.50860400 -0.52188300
C 2.16290900 1.04070000 -0.34762500
H 2.35564300 1.75410600 0.45801800
H 1.97006700 1.59671900 -1.26684900
H 3.04740300 0.41702800 -0.47832500
INTERMEDIATE E2
C -0.18377800 -0.71113000 0.05805100
C 0.64099300 0.52001800 0.03083300
C -0.35361300 1.61039500 -0.13380100
C -1.56230900 1.03755100 -0.17454900
H -0.14178200 2.66650000 -0.19341600
H -2.54778200 1.47462300 -0.24135300
O 0.38262500 -0.26546100 1.26410700
O -1.54522700 -0.32991000 -0.11757800
C 2.08074900 0.65044200 -0.36843400
H 2.58598200 1.38022000 0.27072900
H 2.16325800 0.98899000 -1.40481200
H 2.60180500 -0.30259200 -0.26671300
C 0.07987000 -2.11379300 -0.38857600
H -0.45300200 -2.81046000 0.26387300
H 1.14580900 -2.33321600 -0.32825100
H -0.26493700 -2.26200300 -1.41343200
INTERMEDIATE E3
C -1.19052000 -0.51952500 -0.28232400
C 1.41129500 -0.25473900 -0.11224100
C 0.07138300 -0.05166600 0.52886500
C -0.92188400 0.89381500 -0.10501000
H 0.03439000 -0.08819300 1.61478900
H -0.86613900 -0.91026300 -1.24778000
O 1.51588700 -0.64595300 -1.25550000
O -1.22965000 2.03832600 -0.22470900
C 2.61379500 0.08676800 0.74216700
H 3.52461000 -0.02608900 0.15603700
H 2.65478300 -0.57262400 1.61517600
H 2.53346400 1.11244700 1.11478200
C -2.35320200 -1.22635100 0.38411500
H -2.59634600 -0.77231200 1.34787100

H -2.11472800 -2.27968100 0.55215300
H -3.24513000 -1.17208000 -0.24478700
INTERMEDIATE E4
C 1.83429200 -0.06797500 -0.05344400
C 0.70166500 -0.97719900 -0.17993100
C -0.62189500 -0.62798300 -0.66581300
C -1.64705800 -0.05708200 0.19449000
O -1.39163600 0.24639900 1.35788500
H 0.89968500 -1.99603600 0.14693400
H -0.86204100 -0.80903400 -1.71346400
C 1.62418100 1.39661500 -0.38435800
H 1.15921400 1.51700000 -1.36758200
H 0.95322900 1.84533900 0.35415100
H 2.58334500 1.91156500 -0.36270000
C -3.02709300 0.15487500 -0.40304900
H -3.66422000 0.64175500 0.33358900
H -2.97320000 0.77174600 -1.30496300
H -3.47278700 -0.80290300 -0.68906700
O 2.91566400 -0.49726700 0.33658100
INTERMEDIATE E5(T)
C 1.76032700 -0.07802800 0.03329800
C 0.75889200 -1.12851800 0.08100700
C -0.64216900 -1.06244600 0.15692500
C -1.52344400 -0.02124200 -0.06656800
O -1.18016600 1.21612100 -0.48789400
H 1.19691900 -2.11962400 0.02854600
H -1.13440600 -2.00886100 0.35744000
C 1.54672100 1.25140700 0.56697000
H 2.30970600 1.99428100 0.37156700
H -0.21903500 1.29096200 -0.59627600
H 0.79247900 1.45841400 1.31744900
C -3.00297700 -0.14861500 0.09672200
H -3.51011500 0.08819200 -0.84428600
H -3.28517500 -1.15260200 0.41090700
H -3.36378300 0.56814400 0.84213800
O 2.90883000 -0.34040200 -0.39930700
INTERMEDIATE E5(S)
C -1.71410200 0.02005400 -0.08345000
C 1.40804000 0.07944000 -0.02535200
C 0.64743200 -1.00142400 -0.31608000
C -0.80579700 -1.04229800 -0.44478100
H 1.16605700 -1.93827300 -0.47452900
H -1.21235600 -1.83910700 -1.05830400
O 0.95820100 1.32817300 0.20924300
O -1.68542800 -0.92382400 0.85485000
C 2.90057300 0.02161700 0.07165800
H 3.27789700 -0.97898000 -0.13511300
H 3.21816400 0.32419000 1.07369400
H 3.34547200 0.72790000 -0.63530800
C -2.26065300 1.21064200 -0.30536600
H -2.95089600 1.64587100 0.40569200
H -2.06519900 1.72838000 -1.23445900
H -0.01428200 1.36705000 0.16580900

4.2 Transition States

TS1
C -1.07672700 -0.82378900 -0.11856200
C 1.65790800 -0.07035900 0.17286200
C 0.58469300 0.86178800 0.40965700
C -0.77798800 0.44707000 0.54878400
H 0.80627100 1.91393300 0.55003600
H -0.33859000 -1.30066600 -0.74603300
O 1.50679800 -1.29583300 0.28247000
O -1.69050200 1.09334900 1.09102700
C 3.00839800 0.49804600 -0.23267600
H 3.44933600 1.02337700 0.62110000
H 2.91748000 1.21897700 -1.04855800
H 3.66943800 -0.31624600 -0.52560000
C -2.40315100 -1.40604400 0.03761300
H -2.37358400 -2.04455700 0.93873400
H -2.70874200 -2.03653200 -0.79799400
H -3.11612200 -0.61040900 0.28090600
TS2
C -0.90585300 0.98028100 0.47745000
C 1.41193900 -0.00149400 0.10917000
C -0.04212200 0.13268400 -0.36703200
C -0.89721700 -1.00111100 -0.08580900
H -0.08374200 0.36892000 -1.43677300
H -0.78395600 0.85198500 1.54642900
O 1.76801700 -0.94816700 0.76632500
O -1.74841600 -1.73740400 0.21349300
C 2.30621900 1.15880200 -0.26254900
H 2.78678100 0.93467400 -1.22178500
H 3.08656300 1.27325500 0.48937600
H 1.73915400 2.08484500 -0.36314100
C -2.15450600 1.62038900 -0.04885000
H -2.03105800 1.97717300 -1.07834800
H -2.42367000 2.48893700 0.55927800
H -3.03536100 0.95258500 -0.04025900
TS3
C 0.61630600 -0.66734700 -0.07565700
C 0.00259300 0.74149800 0.19061700
C -1.77997200 0.21896300 0.04958800
C -1.91786100 -1.01669800 -0.07167100
H -2.41317000 1.07921400 0.15863000
H -2.34072900 -1.99364600 -0.14769400
O 0.27555600 1.12234500 1.35728400
O -0.06892800 -1.67870800 -0.14621200
C 0.14857400 1.73916500 -0.97250900
H -0.41243500 2.64326000 -0.72842900
H -0.19867400 1.34050800 -1.93034300
H 1.20218600 2.02277300 -1.06063300
C 2.11143300 -0.75044800 -0.07810900
H 2.44955000 -1.78466800 -0.04610300
H 2.47160900 -0.18882300 0.78696600
H 2.50220100 -0.25851600 -0.97452400
TS4
C -0.81504500 -0.56554200 -0.29978900

C 1.63419600 0.22061000 0.06598900
C 0.93168500 1.23648800 -0.17393300
C -0.78153800 0.98536400 -0.40298200
H 1.15714600 2.28673600 -0.23912400
H -0.86854900 1.30003300 -1.48087100
O 0.18645900 -1.21103300 -0.02904800
O -1.51269200 1.55203800 0.46132500
C 2.75682500 -0.65202500 0.37700500
H 2.56882700 -1.22660500 1.28734000
H 3.64980400 -0.03659000 0.52995900
H 2.95426800 -1.35140500 -0.43888700
C -2.16071600 -1.20375300 -0.42585300
H -2.12483800 -2.26858500 -0.20312900
H -2.54810100 -1.03774000 -1.43616200
H -2.82471500 -0.67016400 0.25915800
TS5
C -0.60756200 -1.05335000 -0.76567500
C 1.70488800 0.61579100 0.15173700
C 0.82378500 1.46865400 0.29190300
C -0.98953400 0.92365200 -0.32816900
H 0.58008100 2.45991300 0.60944500
H -1.07908700 -0.90472500 -1.75678000
O 0.63137600 -1.16120400 -0.69652900
O -1.82572600 1.70497700 -0.41938100
C 2.93395700 -0.15775000 0.09110700
H 2.85354200 -1.04690900 0.71885800
H 3.77987200 0.45046600 0.42723000
H 3.11357800 -0.49515200 -0.93129400
C -1.50894000 -1.70511600 0.27637400
H -1.09835400 -1.55638700 1.27661100
H -1.53093700 -2.78203200 0.07757000
H -2.53419600 -1.32924900 0.23494700
TS6
C -1.68139300 -0.02892400 -0.03986400
C 1.38442700 0.06355900 -0.01141200
C 0.62523600 -1.04570400 -0.38927900
C -0.75683900 -1.05875900 -0.55178800
H 1.17498400 -1.96516500 -0.54760400
H -1.23189800 -1.96519900 -0.90741900
O 0.92010600 1.26015800 0.22596900
O -2.00826200 -0.70676000 0.99011700
C 2.86472900 -0.03431500 0.17492700
H 3.36053300 0.73479500 -0.42313900
H 3.24750600 -1.01653400 -0.09642100
H 3.10746200 0.16885700 1.22252200
C -1.88935300 1.24779600 -0.46243000
H -2.57695100 1.89415700 0.06828200
H -1.56983800 1.53399100 -1.45754500
H -0.08740100 1.32599800 0.09172000
TS7
C 2.32031100 -0.35601200 -0.00317200
C -1.73271500 -0.00127900 0.00344500
C -1.09968500 1.25825700 -0.01569100
C 0.27919000 1.27428000 -0.02452500
H -1.76352100 2.12499100 -0.02220500
H 0.67362000 2.29927300 -0.04066200

O -1.04948100 -1.10678500 0.01166500
O 1.79979200 -1.41212100 -0.03255800
C -3.20838700 -0.19862800 0.01585100
H -3.49121200 -0.77069700 0.90426800
H -3.50328100 -0.79344900 -0.85346000
H -3.73838700 0.75196600 0.00733300
C 3.22190700 0.60391500 0.03545900
H 4.25957700 0.29200400 0.06443600
H 2.96196500 1.64516300 0.03790800
H -0.08496000 -0.88118700 0.00132900
TS8
C 1.26073100 0.04333000 -0.09849500
C 0.57697600 1.33363300 0.27557600
C -0.82428500 1.19887000 0.39401900
C -1.30910900 -0.04162500 -0.03978900
O -0.41154900 -0.89044800 -0.41334700
H 1.12017700 2.25417100 0.12457200
H -1.45406000 1.95986300 0.83831900
C 1.73446300 -0.94885200 0.95535800
H 1.02181700 -0.98281000 1.77699100
H 1.85109100 -1.93926800 0.51567500
H 2.70167600 -0.59553800 1.32358000
C -2.75490100 -0.43417400 -0.09517100
H -2.93991600 -1.30477600 0.54190800
H -3.40734900 0.38133100 0.22139600
H -3.01766600 -0.72304100 -1.11718400
O 1.91417200 0.14582000 -1.15843300
TS9
C 1.71803000 -0.14738100 0.00008400
C 0.74961800 -1.18301800 -0.00015600
C -0.65147100 -1.09830400 0.00034900
C -1.50418900 0.00898100 -0.00009300
O -1.15132100 1.26398800 -0.00056200
H 1.17865000 -2.18048600 -0.00062700
H -1.16749400 -2.05158200 0.00062900
C 1.39052000 1.32557900 0.00047600
H 1.73656200 1.83681800 -0.89926000
H 0.11649800 1.37198800 -0.00030600
H 1.73497600 1.83599600 0.90130000
C -3.00191100 -0.17082900 0.00007000
H -3.43144800 0.31430100 0.88122700
H -3.43188400 0.31735800 -0.87915600
H -3.28335300 -1.22353800 -0.00152300
O 2.94430900 -0.34286700 -0.00027200
TS H-abstraction from O(^{3}P) (bimolecular channel)
C -0.46151500 -0.36437100 -0.04906400
C -0.38392600 0.99304900 -0.06822200
C 1.00606000 1.32464700 -0.03523500
C 1.68267800 0.14865800 0.01104700
O 0.80533700 -0.88594100 0.01115100
H -1.22634200 1.66749300 -0.08207800
H 1.44567700 2.31107100 -0.03381000
C -1.55400600 -1.31651900 -0.03554200
H -1.60253400 -2.12218900 -0.75803500
H -2.11906100 -1.44422200 0.88147800
H -2.79081100 -0.45433400 -0.13342400

C 3.12531100 -0.19873700 0.05749700
H 3.41474800 -0.80679800 -0.80436000
H 3.72677700 0.71137300 0.05119800
H 3.36817800 -0.76520300 0.96104700
O -3.89336800 0.55874600 0.06823700
TS of the dissociatevely photoionizing 1,2-diacetyl ethylene cation
C 1.69624400 -0.12312200 -0.01624900
C -1.48742400 0.07879700 -0.01285800
C -0.64228500 -1.09958400 0.24604600
C 0.70324200 -1.19808000 0.23909600
H -1.20502400 -2.01679600 0.38321000
H 1.14774800 -2.18299200 0.35547200
O -1.07194500 1.25726400 -0.09662200
O 2.78398800 -0.38875400 -0.48080100
C -2.94971900 -0.13776100 -0.19810600
H -3.35551000 -0.59904800 0.71064900
H -3.11362300 -0.85110100 -1.01376200
H -3.46130800 0.79924700 -0.40437900
C 1.45155100 1.30860400 0.31725400
H 2.00637200 2.01902200 -0.29331100
H 1.47801300 1.53262300 1.38731700
H 0.17733000 1.37784200 0.04308800

4.3 Minimum Energy Crossing Points

MECP1 connecting adduct C with intermediate E
C -0.78046800 -0.91041800 -0.44642700
C 1.28996100 0.00948800 -0.16419500
C 0.63304400 1.26627800 -0.04914200
C -0.70384500 1.38850100 0.01291000
H 1.20460800 2.18739800 -0.07273900
H -0.82397900 -0.66719900 -1.50887000
O 0.45324300 -1.08788000 0.06088600
O -1.79949000 1.79691800 0.12308700
C 2.71737100 -0.24325400 0.14625900
H 2.87825900 -0.43333900 1.21751300
H 3.32249900 0.62145300 -0.13379600
H 3.09022000 -1.11214800 -0.40253800
C -1.88545600 -1.63983700 0.21404600
H -1.78883000 -1.58493900 1.30038100
H -1.89174600 -2.69970000 -0.07294500
H -2.84469400 -1.20837400 -0.07948600
MECP2 connecting adduct C with intermediate E1
C -0.88057800 -0.54304200 -0.32366900
C -0.79135100 0.95283500 -0.43154800
C 0.71186800 1.13303000 -0.37070300
C 1.26054000 -0.04271500 -0.04712000
O 0.34191200 -1.05375300 0.04148100
H -1.26423600 1.37336700 -1.33057100
H 1.21835000 2.07947400 -0.47393700
C -2.06778800 -1.33640300 0.05913100
H -1.90560900 -2.39873100 -0.13892000
H -2.29640600 -1.22188100 1.12829900
H -2.94359600 -1.00450200 -0.50316100

C 2.66658700 -0.43842400 0.20641200
H 2.99124900 -1.20096700 -0.50673400
H 3.32441500 0.42738400 0.12747400
H 2.75926400 -0.86072800 1.21073200
O -1.25180000 1.61061500 0.69999300
MECP3 connecting adduct C with intermediate E2
C 1.08854300 -0.35825400 -0.28205200
C -1.16737200 -0.07106100 -0.06659300
C -0.97306200 1.24641500 0.22799600
C 0.29643100 1.79041700 0.03994400
H -1.76642300 1.85428400 0.64698500
H 0.60023900 2.81753600 0.15568100
O -0.13025200 -0.68056400 -0.80440800
O 1.34600200 0.93594600 -0.07147200
C -2.32064700 -0.95632100 0.21421100
H -2.67357400 -1.43841300 -0.70401200
H -3.14446100 -0.38788500 0.65042900
H -2.04913300 -1.75539700 0.91393900
C 1.90225800 -1.36174000 0.44116800
H 2.92321900 -0.99555100 0.56287300
H 1.92559800 -2.30256700 -0.11184300
H 1.50162200 -1.57180200 1.44494300
MECP4 connecting adduct D with intermediate R2
C 0.97162300 -0.04753600 -0.14196900
C 0.49113900 1.37913600 0.01861100
C -0.88837500 1.31951800 0.13539900
C -1.30102300 0.00939300 0.01885100
O -0.22787100 -0.82895800 -0.16756900
H 1.15723800 2.22542000 0.07541800
H -1.55186200 2.15958000 0.29223200
C 1.86031500 -0.55440500 1.04452800
H 1.24255400 -0.46370600 1.93702900
H 2.13701800 -1.59887000 0.89703000
H 2.75192500 0.06381700 1.13945400
C -2.63632500 -0.62844900 0.02026900
H -2.73002700 -1.35928600 0.83053100
H -3.41703300 0.12391000 0.14302200
H -2.81466100 -1.16188400 -0.91942300
O 1.75796100 -0.27790700 -1.20361000
MECP5 connecting intermediate E5(T) with intermediate E5(S)
C 1.74854600 -0.07035400 0.02450000
C 0.74882200 -1.12752100 0.23303600
C -0.63806300 -1.04741700 0.28179400
C -1.48198800 0.01010000 -0.04792100
O -1.09973100 1.21468400 -0.43783600
H 1.17954900 -2.12517200 0.26040900
H -1.16088000 -1.97333400 0.50009300
C 1.56357600 1.18082700 0.67858300
H 2.33295800 1.93750600 0.57954800
H -0.12731600 1.32397800 -0.39769200
H 0.80933500 1.31272500 1.44834200
C -2.96639200 -0.12802400 -0.05595100
H -3.35576300 0.12433500 -1.04674700
H -3.28284400 -1.13655400 0.20637600
H -3.40947900 0.57980400 0.65145000
O 2.74566100 -0.33330400 -0.67291800

4.4 Intermediates electronic structures of the O(^{3}P) addition reaction coordinates

O(^{3}P)-C1: 2.0 Angstrom
C -0.89073600 -0.04884500 -0.25012600
C -0.47591700 1.28249000 -0.41291200
C 0.91950700 1.29013800 -0.24907900
C 1.30361400 -0.01574100 -0.08224500
O 0.22370600 -0.82950000 -0.14606500
H -1.13921600 2.12312000 -0.54642800
H 1.57921700 2.14492000 -0.24266300
C -2.12406100 -0.73505000 -0.72467600
H -2.00424300 -1.05481600 -1.76398900
H -2.33256500 -1.61492300 -0.11384300
H -2.97261800 -0.05468900 -0.66016000
C 2.61463200 -0.66114500 0.15499000
H 2.82504900 -1.41405600 -0.60984100
H 3.40985700 0.08463100 0.13783300
H 2.62847400 -1.16267200 1.12686900
O -1.48322900 0.11417600 1.65312900
O(^{3}P)-C1: 2.5 Angstrom
C -0.88248100 -0.39828900 -0.29280000
C -0.59769700 0.75896500 -0.96496200
C 0.80997900 0.96760800 -0.82669700
C 1.27965000 -0.06836600 -0.08833300
O 0.25690400 -0.90999700 0.22811600
H -1.30770200 1.37355800 -1.49593200
H 1.39234800 1.79048200 -1.21251800
C -2.12929800 -1.17040300 -0.07985300
H -2.07027000 -2.15309000 -0.55663100
H -2.31190500 -1.32288400 0.98669000
H -2.97761400 -0.63134800 -0.50262200
C 2.62423700 -0.43912500 0.41480900
H 2.94159700 -1.40823300 0.01935300
H 3.35474900 0.31162700 0.11141900
H 2.62987300 -0.50539100 1.50615500
O -1.29158100 1.49036500 1.29327200
O(^{3}P)-C1: 3.0 Angstrom
C -1.29971100 -0.04426100 -0.07617700
C -0.84805700 1.03487200 -0.76558900
C 0.55505100 0.84570900 -0.93561200
C 0.86401100 -0.33740300 -0.31851800
O -0.26595300 -0.88674400 0.18878500
H -1.44400100 1.86869100 -1.10353000
H 1.25762100 1.49927900 -1.42912300
C -2.63386000 -0.45592900 0.42285700
H -2.94492700 -1.40729800 -0.01926200
H -2.62356900 -0.57957300 1.50934900
H -3.37723900 0.30056900 0.16821100
C 2.10673300 -1.13929100 -0.21229900
H 2.03865200 -2.04622600 -0.82141200
H 2.95858500 -0.55222000 -0.55560600
H 2.28864300 -1.44065200 0.82214800
O 1.43860700 1.25365000 1.40387200

O(^{3}P)-C1: 3.5 Angstrom
C 0.65527700 -0.78194100 -0.00882800
C 0.29958100 -0.64560300 1.29113400
C -1.02245000 -0.08684200 1.29429900
C -1.37321200 0.07552100 -0.00395700
O -0.35734300 -0.34487500 -0.80658000
H 0.90278600 -0.91125500 2.14673100
H -1.62939200 0.16018700 2.15282400
C 1.87591500 -1.27870400 -0.69230700
H 1.64896700 -2.12342000 -1.34911200
H 2.33526500 -0.49562200 -1.30246000
H 2.60726600 -1.60802600 0.04725600
C -2.58952800 0.59023900 -0.68196100
H -3.04464900 -0.17590400 -1.31636100
H -3.32578300 0.89995700 0.06121700
H -2.35866400 1.45204800 -1.31479300
O 2.33118100 2.29062700 0.01713200
O(^{3}P)-C1: 4.0 Angstrom
C 0.00000000 0.00000000 0.00000000
C 0.00000000 0.00000000 1.35462451
C 1.37652477 0.00000000 1.76103532
C 2.11214046 -0.00010667 0.62361149
O 1.28264907 -0.00042085 -0.45567995
H -0.87295107 0.00135552 1.99057102
H 1.76404768 0.00024123 2.76914983
C -1.07249298 -0.01087761 -1.02640990
H -1.00532717 0.86202275 -1.68213671
H -1.01197527 -0.90491229 -1.65374253
H -2.04992655 0.00038401 -0.54187237
C 3.57019121 0.00606252 0.34414969
H 3.86207097 0.89520104 -0.22225481
H 4.12788263 0.00005204 1.28183486
H 3.86842718 -0.87130656 -0.23702767
O -0.37830072 -3.98023119 -0.12102993
O(^{3}P)-C1: 4.5 Angstrom
C 0.29503200 -1.03488700 -0.00619900
C -0.00086800 -0.79298500 1.29339100
C -1.09487100 0.13607100 1.29499000
C -1.38354100 0.39074100 -0.00373100
O -0.54183200 -0.31786800 -0.80518300
H 0.49682600 -1.22360900 2.14974200
H -1.59823100 0.55703000 2.15283100
C 1.30948300 -1.87719800 -0.68831200
H 0.83864000 -2.61784100 -1.34115100
H 1.98103100 -1.27012300 -1.30230700
H 1.91013800 -2.40742000 0.05220000
C -2.39125300 1.24334100 -0.68317100
H -3.05621900 0.64609000 -1.31379500
H -2.99945000 1.76236800 0.05913400
H -1.91417200 1.99386500 -1.32003500
O 3.53402400 2.08901000 0.00788000
O(^{3}P)-C1: 5.0 Angstrom
C -0.06462400 0.95082900 0.01115300
C 0.21093300 0.67523200 1.30755100
C 1.27523300 -0.28771100 1.29660200
C 1.57429900 -0.51174300 -0.00521000

O 0.75990200 0.23480600 -0.79451600
H -0.26203900 1.12894900 2.16712700
H 1.74986400 -0.75431300 2.14945000
C -0.97657300 1.91421600 -0.66375100
H -0.39182800 2.76150900 -1.05739600
H -1.50773500 1.44042700 -1.49774000
H -1.71418000 2.30889700 0.03872000
C 2.54659600 -1.39374300 -0.70197000
H 3.10804500 -0.83623600 -1.45704900
H 3.25941400 -1.80969800 0.01419200
H 2.04545600 -2.22642700 -1.20674300
O -4.97017300 -1.49675500 -0.03258600
O(^{3}P)-C2: 2.0 Angstrom
C -0.89904600 -0.48747000 -0.22288800
C -0.70696400 0.78935300 -0.71968600
C 0.72057600 1.00675400 -0.68182600
C 1.25843800 -0.07910400 -0.08997100
O 0.27990600 -0.99497700 0.19760700
H -1.42657000 1.34987400 -1.29472600
H 1.24955200 1.89040800 -1.00322600
C -2.11339600 -1.29823100 0.01114100
H -2.01583600 -2.29243500 -0.43370800
H -2.29090600 -1.42506400 1.08320900
H -2.98262800 -0.80438900 -0.42391000
C 2.63977900 -0.45744400 0.29098200
H 2.92958300 -1.40436400 -0.17250700
H 3.33969200 0.31430100 -0.03078300
H 2.72917400 -0.57427900 1.37445200
O -1.14595300 1.75782700 0.97422900
O(^{3}P)-C2: 2.5 Angstrom
C -0.87674400 -0.35372800 -0.31414000
C -0.57326600 0.82384500 -0.94380800
C 0.83333300 1.01216100 -0.78675000
C 1.28710100 -0.05840400 -0.08656600
O 0.25498500 -0.90048700 0.18884100
H -1.27507800 1.46824000 -1.44988500
H 1.42791000 1.84303100 -1.13503400
C -2.12948400 -1.13062200 -0.15908500
H -2.07416400 -2.07890100 -0.70149800
H -2.31714000 -1.35393300 0.89394100
H -2.97248500 -0.55819400 -0.54706500
C 2.62360600 -0.46088700 0.41352600
H 2.93499200 -1.41762500 -0.01529600
H 3.36402600 0.29342200 0.14517800
H 2.61780900 -0.56837600 1.50158400
O -1.34162900 1.32275500 1.38228400
O(^{3}P)-C2: 3.0 Angstrom
C -0.80913200 -0.27963300 -0.42398300
C -0.43580200 0.88375700 -1.03560500
C 0.95857500 1.04812900 -0.77623000
C 1.34136200 -0.02811300 -0.04161600
O 0.27710100 -0.84496100 0.16542800
H -1.08910200 1.54320100 -1.58703700
H 1.59369600 1.86443000 -1.08615700
C -2.06375300 -1.07377300 -0.41686200
H -1.96161100 -1.97377700 -1.03100400

H -2.32746300 -1.38908000 0.59580500
H -2.88331400 -0.47490100 -0.81496000
C 2.62853000 -0.44361000 0.56740900
H 2.95857400 -1.41086900 0.17787700
H 3.39996200 0.29596900 0.34952700
H 2.53486100 -0.53555700 1.65301500
O -1.77013600 1.02496600 1.64760400
O(^{3}P)-C2: 3.5 Angstrom
C 0.76569900 -0.65478700 -0.08105500
C 0.36710300 -0.77074900 1.21149900
C -1.00424700 -0.35419500 1.25360800
C -1.34164400 -0.01859600 -0.01499200
O -0.27179800 -0.19944100 -0.83606000
H 0.98011700 -1.10569900 2.03524000
H -1.65141100 -0.30827000 2.11690500
C 2.03019800 -0.96199700 -0.79636200
H 1.87131100 -1.72038500 -1.56846000
H 2.44587600 -0.07250400 -1.27630800
H 2.76909300 -1.34315800 -0.08979900
C -2.58802000 0.48667900 -0.64279300
H -2.95486900 -0.20190500 -1.40944400
H -3.36445400 0.59915700 0.11530800
H -2.42851800 1.45933900 -1.11693300
O 1.89158900 2.24135300 0.28781700
O(^{3}P)-C2: 4.0 Angstrom
C 0.42198300 -1.03469100 0.13005900
C 0.45732600 -0.28002800 1.25466800
C -0.67435600 0.60016100 1.18918800
C -1.31558100 0.31468100 0.03062700
O -0.65500600 -0.68043100 -0.62262700
H 1.20245300 -0.33550500 2.03448500
H -0.97201300 1.34335000 1.91404800
C 1.29772500 -2.10384200 -0.41213900
H 0.74765400 -3.03844000 -0.55469900
H 1.72437800 -1.81789600 -1.37786900
H 2.11847500 -2.29457900 0.28102800
C -2.54332900 0.84089400 -0.61724300
H -3.31834600 0.07189500 -0.68733000
H -2.94128600 1.67365300 -0.03547300
H -2.33669300 1.19848900 -1.62983600
O 2.89410300 2.32742900 -0.55178800
O(^{3}P)-C2: 4.5 Angstrom
C -0.13363800 1.14135800 0.10110400
C -0.26178500 0.48525400 1.27920300
C 0.65048700 -0.62186100 1.23027400
C 1.26803400 -0.55687700 0.02644200
O 0.79645500 0.51363900 -0.66975300
H -0.92698900 0.75528800 2.08617100
H 0.81823700 -1.36959200 1.99122100
C -0.77258500 2.34969300 -0.47873800
H -0.03083300 3.12216900 -0.70087600
H -1.29696200 2.11462600 -1.40950700
H -1.49643200 2.76177000 0.22583900
C 2.29811800 -1.38760600 -0.64634700
H 3.19320800 -0.80396800 -0.88020100
H 2.59125500 -2.21405900 0.00318900

H 1.91936500 −1.80727900 −1.58279900
O −3.67928500 −1.89097800 −0.43083100
O(^{3}P)−C2: 5.0 Angstrom
C 0.12048900 1.17710900 0.08035700
C −0.05578900 0.59358000 1.28990900
C 0.65601800 −0.65187100 1.24878900
C 1.21331900 −0.73478200 0.01711600
O 0.89378800 0.37562700 −0.70283700
H −0.62333200 0.99927000 2.11439300
H 0.73763500 −1.38906700 2.03385000
C −0.34153800 2.45358800 −0.52058100
H 0.50243400 3.09291800 −0.79578300
H −0.93259100 2.27663600 −1.42373800
H −0.96266400 2.99697800 0.19297700
C 2.05793700 −1.75097700 −0.65976600
H 3.01006300 −1.32242600 −0.98546800
H 2.27009600 −2.57208000 0.02665200
H 1.55919400 −2.16241300 −1.54214200
O −4.32671900 −1.43058900 −0.34162300

5 Harmonic Vibrational Frequencies

The harmonic vibrational frequencies corresponding to every saddle point and MECP are showed in Table 1, while those ones of the constrained optimization intermediate structures referring to the O(^{3}P) addition reaction coordinate are listed in Table 2. As regards MECP harmonic vibrational frequencies, these are calculated by using a semi-empirical Hamiltonian to calculate the effective Hessian matrix of the local mixed-spin state. [6]

TS1	TS2	TS3	TS4	TS5	TS6	TS7	TS8	TS9	MECP1	MECP2	MECP3	MECP4	MECP5
25.9	54.1	82.9	56.3	46.1	95.7	6.6	87.3	45.0	45.5	81.1	32.4	90.1	98.5
70.9	90.1	128.8	109.5	74.5	120.9	50.1	123.9	100.3	69.3	136.6	160.5	143.1	110.6
127.1	102.2	177.7	139.1	124.0	132.1	58.6	213.1	124.5	139.9	187.3	173.9	169.4	131.6
138.1	125.4	197.7	162.5	145.4	235.2	123.7	217.3	302.0	159.3	198.6	207.4	212.6	200.1
268.1	139.3	220.4	200.4	169.9	297.6	187.5	291.4	315.0	178.0	232.9	274.8	294.8	225.5
295.1	186.1	240.3	240.4	203.2	408.2	194.9	300.3	346.0	244.3	286.1	359.4	346.4	301.4
348.6	308.7	293.2	309.8	237.5	430.6	323.4	330.8	389.8	302.4	383.0	411.0	384.9	390.9
396.0	326.8	363.1	333.2	262.3	469.7	346.6	420.0	400.8	394.9	427.4	459.5	462.1	466.3
530.0	362.6	390.8	410.0	355.3	550.8	415.6	468.0	456.7	406.1	576.4	491.7	522.7	500.3
584.8	444.2	542.9	545.4	384.8	632.0	440.7	523.9	531.0	458.5	601.3	539.1	606.5	558.2
587.5	555.9	566.9	560.6	436.0	667.7	561.0	557.8	625.5	492.1	657.7	594.4	620.7	574.2
653.4	609.8	591.9	580.6	460.3	743.5	584.1	584.6	660.6	530.1	670.9	653.7	689.0	628.0
670.4	617.0	609.8	639.2	501.8	755.5	610.8	673.3	748.2	636.3	804.6	744.4	742.6	725.2
802.2	833.4	676.6	746.7	544.0	788.6	633.7	746.2	779.4	707.6	829.9	817.1	812.0	789.4
851.4	886.6	707.5	782.6	645.7	842.7	658.9	786.8	787.5	818.1	928.7	896.2	896.9	804.0
956.8	939.4	773.2	908.8	823.6	929.9	877.7	952.7	907.5	884.7	965.0	925.9	899.9	839.8
967.9	978.0	851.0	938.0	882.4	979.8	908.5	971.8	921.7	940.8	986.3	981.5	936.6	863.5
994.8	1013.2	903.0	987.1	937.6	1012.5	962.8	1008.2	1028.4	1009.4	1018.8	1015.6	952.3	949.4
1034.0	1043.2	952.0	1034.0	960.2	1017.0	973.4	1020.4	1030.0	1051.7	1041.3	1045.6	990.0	963.0
1076.4	1082.3	991.1	1054.0	1037.8	1033.2	1025.7	1040.0	1045.8	1066.1	1082.6	1061.9	1044.5	1025.6
1142.4	1152.3	1044.8	1062.2	1058.7	1061.2	1061.0	1058.2	1064.5	1156.5	1112.1	1107.3	1054.6	1043.3
1179.8	1184.5	1057.9	1161.4	1084.1	1184.6	1062.8	1095.2	1171.4	1160.9	1200.1	1150.5	1059.4	1059.4
1224.9	1202.4	1117.3	1218.2	1115.0	1231.9	1134.8	1229.6	1220.3	1239.3	1223.4	1257.3	1152.7	1185.3
1342.2	1288.5	1235.6	1338.7	1362.3	1301.0	1175.8	1312.4	1226.0	1283.1	1296.1	1299.7	1249.0	1245.5
1375.6	1383.2	1376.6	1374.0	1392.2	1395.4	1308.8	1370.9	1273.0	1401.8	1331.7	1339.1	1289.2	1339.6
1383.4	1386.2	1377.4	1403.3	1403.7	1404.1	1335.1	1397.3	1383.2	1427.1	1340.6	1419.3	1365.7	1400.1
1415.9	1416.6	1454.0	1424.5	1455.4	1440.1	1401.6	1411.9	1404.8	1430.3	1424.4	1421.7	1426.7	1430.0
1448.3	1461.3	1462.0	1456.0	1470.8	1459.3	1411.8	1426.0	1426.6	1465.6	1436.9	1436.9	1431.8	1472.6
1457.1	1475.1	1472.1	1461.3	1473.9	1466.9	1452.5	1466.9	1433.4	1485.3	1491.2	1484.5	1480.6	1488.8
1467.8	1483.1	1473.5	1465.3	1481.7	1473.0	1470.0	1469.7	1467.5	1494.6	1494.9	1485.2	1489.0	1490.7
1479.9	1502.5	1494.7	1475.9	1571.9	1531.8	1536.0	1471.2	1473.1	1505.7	1499.7	1500.2	1492.6	1520.2
1597.8	1792.3	1683.3	1704.3	1989.7	1561.0	1549.2	1482.3	1492.9	1516.2	1511.6	1510.9	1494.5	1556.9
1634.9	2052.4	1807.2	1939.9	2082.6	1714.4	2121.3	1523.0	1527.6	2062.7	1687.6	1567.2	1565.5	1576.2
2962.2	2907.5	3019.9	2669.2	2894.3	2733.8	3025.0	3024.6	1631.1	3007.3	2988.4	2982.0	3042.2	2766.8
3030.8	3017.7	3037.4	3024.7	3024.0	3039.1	3040.8	3044.3	3032.6	3015.2	3026.1	3032.7	3061.3	3059.8
3036.1	3027.3	3088.2	3035.6	3029.8	3093.2	3076.3	3076.3	3072.2	3097.0	3056.9	3084.8	3109.1	3120.3
3091.2	3030.6	3102.8	3088.6	3087.4	3139.7	3094.9	3113.3	3085.6	3101.6	3110.1	3102.8	3143.8	3151.2
3124.9	3069.2	3112.8	3097.8	3099.5	3144.8	3148.7	3122.7	3129.1	3120.1	3120.9	3140.7	3153.5	3172.9
3141.2	3102.7	3150.5	3099.5	3114.0	3179.5	3161.3	3154.5	3142.5	3139.6	3147.0	3157.0	3185.2	3191.4
3183.4	3142.5	3305.0	3150.9	3118.7	3197.2	3309.2	3192.3	3157.6	3150.8	3163.1	3225.0	3250.8	3206.0
3239.3	3172.9	3403.1	3280.1	3368.1	3233.6	3384.9	3228.9	3177.9	3198.8	3287.4	3288.2	3291.4	3260.5

Table 1 Harmonic vibrational Frequencies (cm^{-1}) of the transition states allocated on the PES and MECPs.

2 Å(C1)	2.5 Å(C1)	3 Å(C1)	3.5 Å(C1)	4 Å(C1)	4.5 Å(C1)	5 Å(C1)	2 Å(C2)	2.5 Å(C2)	3 Å(C2)	3.5 Å(C2)	4 Å(C2)	4.5 Å(C2)	5 Å(C2)
123.0	71.5	70.3	17.6	21.8	14.3	19.1	84.5	73.0	56.4	27.5	15.3	11.2	8.3
159.0	129.4	105.6	29.8	39.2	30.5	29.9	125.1	150.3	81.2	68.1	23.0	16.7	11.2
164.9	148.8	159.2	96.6	132.7	160.0	145.3	165.6	152.2	134.9	174.0	121.8	139.1	130.7
183.8	174.6	176.9	118.4	142.8	173.3	188.3	170.9	177.1	137.8	183.1	151.8	152.7	144.7
219.6	183.5	186.2	184.8	189.2	184.7	223.6	195.7	191.4	194.0	198.3	187.2	185.1	185.6
263.7	259.1	258.0	256.1	259.7	257.1	258.5	261.4	258.4	259.0	265.1	255.6	257.2	254.6
280.2	267.5	300.0	274.7	271.5	269.5	282.6	279.0	293.2	268.7	270.7	276.8	278.2	279.0
405.1	402.4	398.1	395.3	403.1	400.5	404.9	408.4	400.7	400.4	407.5	396.1	399.1	398.1
492.6	523.0	585.4	601.1	593.1	575.0	601.3	527.3	525.5	556.7	573.9	597.2	604.3	606.4
615.5	620.4	619.0	612.6	614.1	606.6	630.1	616.7	615.3	624.4	621.0	613.6	609.6	611.5
626.8	636.1	626.1	641.4	635.1	640.6	641.9	633.8	622.7	646.9	649.4	638.8	627.9	639.5
699.6	705.6	694.3	699.9	698.8	705.5	699.7	702.3	648.8	705.2	684.2	695.5	696.3	698.0
763.0	801.7	723.1	800.6	795.1	803.9	806.3	806.4	700.0	764.1	699.2	780.9	776.9	775.6
872.0	854.0	827.6	843.2	839.0	848.5	850.6	901.3	813.9	834.3	826.2	832.1	823.4	826.0
948.4	961.4	949.7	951.5	936.0	957.3	896.3	954.7	943.1	943.8	962.2	949.0	942.0	923.4
972.5	985.1	974.6	971.6	971.6	989.9	969.5	969.9	974.7	965.9	980.2	979.9	976.4	967.8
998.7	1022.0	1004.2	1008.8	1002.6	1005.8	999.6	1013.5	1014.1	1015.5	1001.6	1004.9	994.5	1000.3
1021.4	1030.9	1026.6	1021.6	1019.2	1039.0	1018.8	1040.2	1030.0	1042.4	1046.0	1033.5	1027.2	1022.7
1040.9	1042.0	1032.6	1042.1	1031.0	1047.9	1043.7	1046.9	1033.2	1045.0	1051.1	1034.4	1032.0	1024.4
1045.8	1050.8	1043.8	1044.7	1047.2	1052.0	1051.7	1062.1	1045.8	1066.1	1073.0	1059.3	1051.1	1056.8
1066.1	1071.5	1060.6	1073.3	1054.9	1076.9	1077.3	1077.7	1068.1	1075.6	1083.2	1070.3	1058.5	1064.4
1223.5	1225.1	1211.4	1181.8	1228.7	1108.8	1221.2	1234.1	1219.4	1235.3	1218.0	1191.9	1199.8	1210.8
1231.4	1257.1	1248.2	1211.1	1260.5	1243.5	1251.2	1244.8	1232.8	1263.2	1242.9	1224.8	1215.5	1219.8
1287.1	1264.9	1255.4	1263.9	1275.2	1268.2	1274.8	1282.8	1262.1	1271.1	1275.2	1246.7	1242.1	1238.4
1417.8	1397.7	1375.3	1369.7	1357.7	1390.5	1292.5	1394.1	1386.8	1409.3	1387.7	1364.2	1376.9	1376.9
1419.4	1432.5	1385.8	1392.5	1362.6	1431.4	1403.0	1436.2	1417.9	1424.3	1435.2	1423.7	1402.4	1403.3
1434.5	1433.3	1422.7	1433.1	1402.5	1436.6	1439.4	1439.5	1425.1	1436.8	1444.9	1430.3	1415.6	1414.2
1476.4	1495.3	1439.1	1437.6	1436.0	1497.1	1447.6	1497.5	1470.0	1489.4	1480.3	1465.8	1461.6	1468.2
1493.3	1495.6	1467.6	1476.0	1442.3	1498.3	1463.9	1497.8	1489.7	1495.3	1501.2	1488.0	1475.9	1470.6
1494.1	1508.7	1490.0	1494.5	1498.1	1508.0	1493.9	1507.1	1491.7	1505.6	1511.6	1495.2	1499.0	1487.5
1506.5	1515.6	1493.7	1508.1	1507.3	1514.6	1512.3	1516.0	1503.5	1515.1	1520.2	1502.4	1502.2	1491.3
1521.2	1554.0	1572.4	1514.0	1619.4	1616.3	1635.0	1579.9	1581.2	1559.8	1626.2	1578.2	1605.1	1608.7
1600.9	1660.8	1651.0	1668.3	1675.7	1683.5	1686.9	1683.5	1631.8	1652.5	1678.8	1662.9	1661.6	1665.0
3058.0	3057.8	2866.2	2910.4	3009.1	3052.1	2445.2	3054.5	3008.1	3054.2	3042.9	3020.8	2931.8	2986.4
3065.3	3058.9	2929.4	3035.0	3012.5	3053.2	2938.1	3059.4	3049.3	3055.5	3050.5	3052.9	2980.3	2998.2
3120.1	3120.3	3045.3	3047.1	3086.2	3112.4	3029.6	3116.4	3061.1	3116.3	3108.7	3091.8	3042.8	3053.5
3138.1	3123.7	3070.5	3108.3	3086.7	3112.9	3080.4	3122.1	3111.9	3118.1	3111.5	3099.8	3056.8	3066.7
3161.7	3157.5	3094.1	3130.5	3137.8	3151.4	3096.4	3159.1	3146.9	3153.6	3136.0	3112.9	3085.6	3074.2
3171.4	3157.6	3124.5	3141.4	3139.6	3152.7	3115.5	3160.5	3148.6	3158.6	3145.5	3146.2	3098.1	3084.5
3264.1	3272.2	3216.1	3236.8	3255.1	3251.8	3199.1	3266.5	3268.0	3250.0	3172.5	3203.1	3119.0	3091.7
3285.5	3287.9	3263.4	3258.8	3269.0	3268.6	3231.8	3281.3	3281.3	3270.5	3263.0	3232.4	3241.1	3243.6

Table 2 Harmonic vibrational frequencies (cm^{-1}) of the constrained optimization intermediate structures. C1 and C2 in the parantheses refer to the reaction coordinate of the approaching O(^{3}P) to carbon C1 and carbon C2 in order to form adduct D and C, respectively.

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