Supporting Material for

'Femtosecond Time-Resolved Photoelectron

Spectroscopy of the Benzyl Radical'

1   Rydberg orbitals

The exponents α_i for the additional s-type Gaussians are computed according to the recipe developed by Kaufmann et.al. in Ref.:[1]

$$\alpha_i = \left(\frac{Z}{2n}\right)^2 \frac{1}{(0.584342i + 0.424483)^2} \qquad \text{for } i = 1, \ldots, n \tag{1}$$

Since the Rydberg series converges to the singly positively charged cation, we choose $Z = +1$. For $n = 3$, we obtain 3 exponents (and thus 3 additional s-like primitive Gaussian basis functions on atom C1): $\alpha_1 = 0.02729391, \alpha_2 = 0.01094397, \alpha_3 = 0.00585838$. These exponents are optimized for representing the $3s$-Rydberg orbital of the hydrogen.

The exponents for the additional p-Rydberg orbitals ($Z = 1, n = 3, l = 1$) are generated in a similar way.

The following listing contains a python script for generating the exponents of a Rydberg orbital with quantum numbers (n, l):

Listing 1: Kaufmann_exponents.py

```
#!/usr/bin/env python
"""
```

```python
Generate a list of exponents for a set of Gaussians that should approximate
a Rydberg orbital (n,l) of an atom with charge Z


Reference:


    Kaufmann ,~K.;\ \ Baumeister ,~W.;\ \ Jungen ,~M.
    Universal Gaussian basis sets for an optimum representation
    of Rydberg and continuum wavefunctions.
    J. Phys. B: At. Mol. Opt. Phys. 22 (1989), 2223-2240.
"""


# a_l and b_l as defined in Table 2
a = {0: 0.584342, 1: 0.452615, 2: 0.382362, 3: 0.337027, 4: 0.304679}
b = {0: 0.424483, 1: 0.309805, 2: 0.251333, 3: 0.215013, 4: 0.189944}


l2spec = {0: 'S', 1: 'P', 2: 'D', 3: 'F'}


if __name__ == "__main__":
    import sys
    if len(sys.argv) < 5:
        print "Usage: %s I Z n l" % sys.argv[0]
        print " generate optimum basis set for Rydberg orbital on center I"
        print " with quantum numbers (n,l) and central charge Z"
        exit(-1)


    I = int(sys.argv[1])
    Z = float(sys.argv[2])
    n = int(sys.argv[3])
    l = int(sys.argv[4])


    print "Uncontracted basis\n"
    exponents = []
    # optimium Gaussian exponents according eqn. 17
```

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```
    for i in range(1, n+1):
        ex = (Z/(2.0*n))**2 / (a[l]*i + b[l])**2
        exponents.append(ex)


    print "%d     0" % I
    for ex in exponents:
        print "%s     1     1.0" % l2spec[l]
        print "                    %10.8f     1.0000000" % ex
    print "****"
```
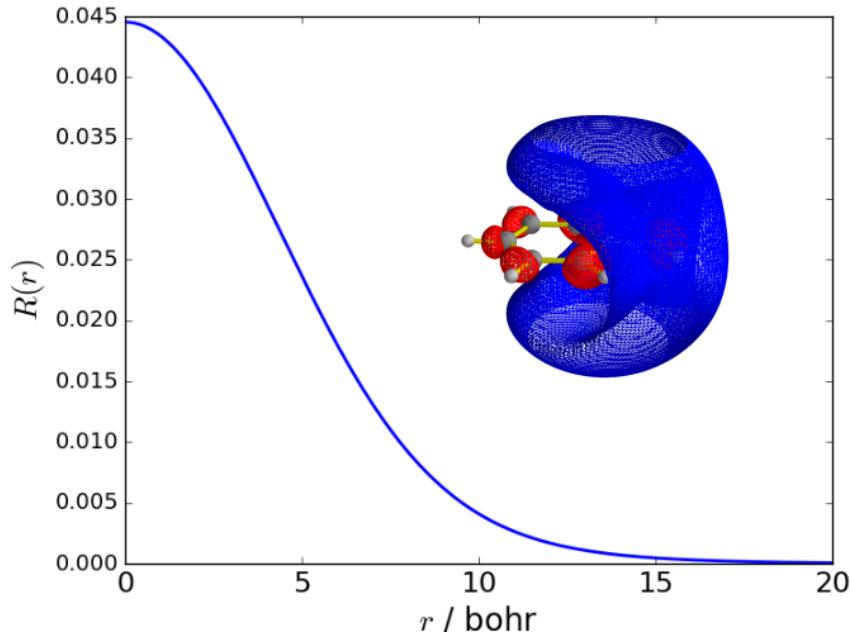

Figure 1: Radial wavefunction of the s-Rydberg orbital. The coefficients of the 3 diffuse primitive Gaussians were singled out from the MCSCF-MO coefficients of the s-Rydberg orbital.

2 Character of the electronic states

To identify the character of the electronic states, the diagonal elements the density matrices for each excited state were subtracted from the diagonal elements of the ground state density

matrix. These differences in occupation numbers are depicted in Fig.2.
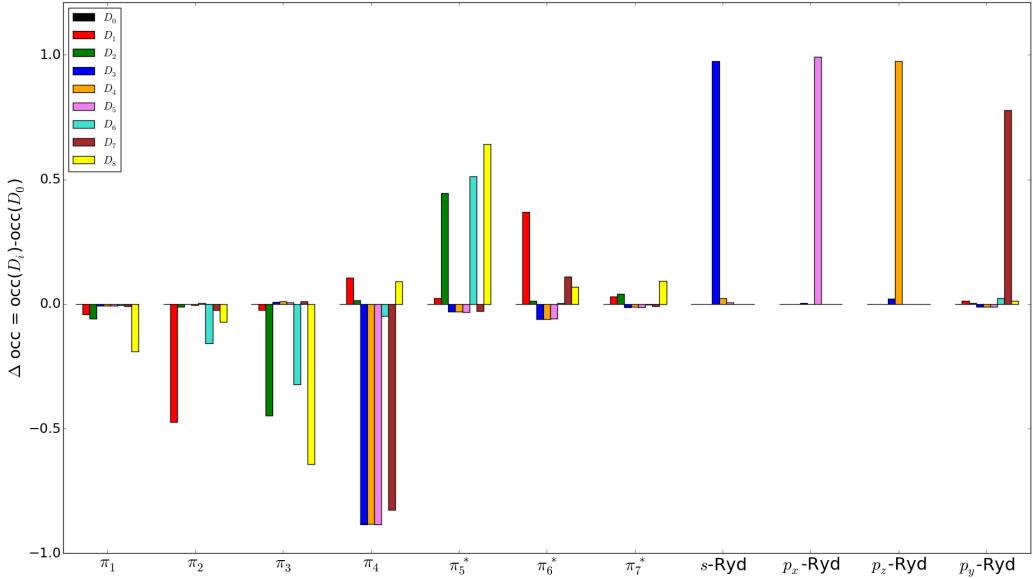
Figure 2: **SA-9-CASSCF(7,11)/aug-cc-pVDZ.** Differences of the diagonal elements of the density matrices between excited states and the ground state.

3   TD-DFT

Since EOMCCSD or CASSCF+MRCI calculations are very time-consuming for running non-adiabatic MD-simulations, we tried to identify a DFT-based electronic structure method, that agrees reasonably well with the EOMCCSD results. Unfortunately all functionals we tested either produced excitation energies that were too low by over 1 eV and/or failed to give the expected relative ordering of valence and Rydberg states. The s-Rydberg state is predicted erroneously to lie approximately 0.5 eV above the $2\ ^2A_2$ state (see Table 1). The failure of DFT is probably partly due to the problem of spin-contamination that befalls open-shell systems. In particular with long-range corrected or hybrid functionals, that are supposed to improve the description of Rydberg states, the $\langle S^2 \rangle$-value deviates considerably from the 0.75 expected for a spin-doublet. For instance for the $2\ ^2A_2$ state, $\langle S^2 \rangle$ increases

from the acceptable value of 0.790 for PBE to 0.937 for the hybrid PBE0 and to even 1.347 for the long-range corrected LC-PBE functional.

Table 1: TD-DFT/aug-cc-pVDZ excitation energies and oscillator strengths (in brackets) for different choices of the functional. In all cases the s-Rydberg state is higher in energy than the $\pi\pi^*$ state.

State	PBE	PBE0	LC-PBE	B3LYP	CAM-B3LYP	ωB97X
$1\ ^2B_2$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$1\ ^2A_2$	2.8389 (0.0003)	3.2942 (0.0002)	3.9310 (0.0002)	3.1350 (0.0003)	3.4580 (0.0002)	3.5905 (0.0002)
$2\ ^2B_2$	3.2146 (0.0018)	3.4136 (0.0027)	3.6364 (0.0032)	3.3611 (0.0024)	3.4703 (0.0027)	3.5240 (0.0036)
$1\ ^2A_1$ (s-Ryd.)	3.9392 (0.0028)	4.5131 (0.0038)	5.6370 (0.0047)	4.2131 (0.0034)	4.6423 (0.0042)	5.1469 (0.0050)
$2\ ^2A_2$ ($\pi\pi^*$)	3.4108 (0.0184)	3.9512 (0.0284)	4.5352 (0.0396)	3.7673 (0.0260)	4.1170 (0.0345)	4.2612 (0.0390)

4 Anisotropy parameters β for ionization from a Rydberg orbital

The angular distribution of photoelectrons that are ejected from an ensemble of isotropically oriented molecules using linearly polarized light is given by

$$\text{PAD}(\theta) = \frac{\sigma(\text{eKE})}{4\pi} \left[1 + \beta(\text{eKE})\frac{1}{2} \left(3\cos(\theta)^2 - 1 \right) \right] \tag{2}$$

where σ is the total ionization cross section and β is the anisotropy parameter ($\beta \in [-1, 2]$), and θ is the angle between the light polarization and the momentum vector of the photoelectron. For atoms β can be calculated using the Cooper-Zare formula.[2] The respective β-curves for the hydrogen atom are shown in fig.3. We use this graph to analyze the photoangular distributions of the benzyl radical, since we attribute the strong photoelectron signal to low-lying Rydberg states, which asymptotically resemble the orbitals of atomic hydrogen. s-orbitals have $\beta = 2$, whereas for a p-orbital β depends strongly on the photokinetic energy. To distinguish an s- from a p-Rydberg orbital one would have to measure the photoangular distribution for a range of kinetic energies close to the inoization threshold, where the β-curve for a p-Rydberg orbital rises steeply. The anisotropy parameter for a 3p-orbital

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changes particulary strongly around eKE = 0-1 eV, where most of the photoelectrons from the benzyl radical are detected. Therefore the photoelectrons most likely originate from an s-Rydberg orbital, but it is not possible to exclude contribution from p-Rydberg states without varying the wavelength of the ionizing radiation.
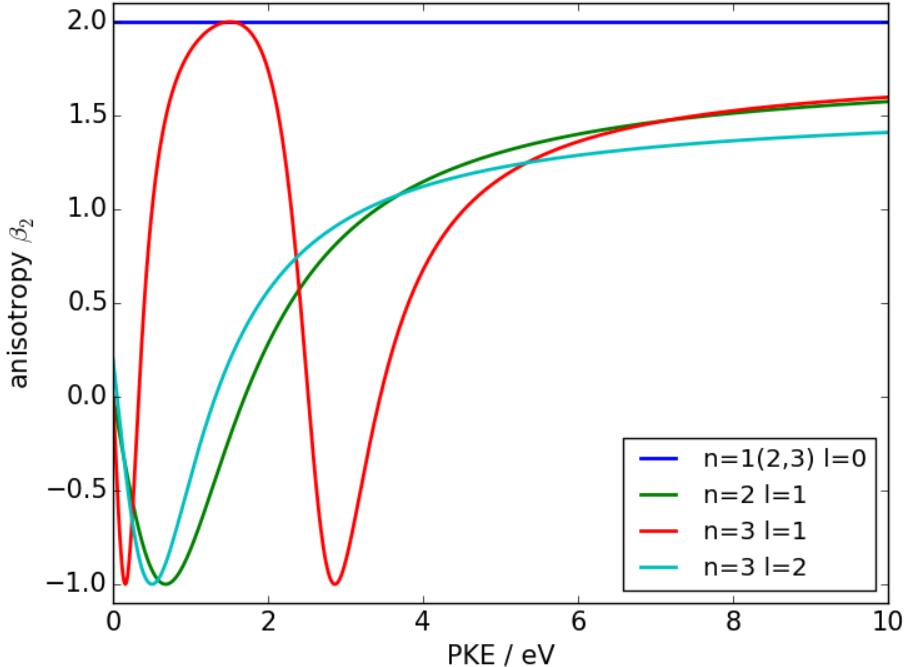
Figure 3: **Cooper-Zare formula:** [2] Dependence of the anisotropy parameter β on the kinetic energy of the photoelectron for ionization from different orbitals of the hydrogen atom with linearly polarized light.

5   CASSCF + MRCI

The following MOLPRO script performs the **SA-9-CASSCF(7,11)+MRCI/(aug-cc-pVDZ + s-,p-Rydberg)** calculation:

Listing 2: MOLPRO input deck

```
***, SA-9-CASSCF(7,11)+MRCI/(aug-cc-pVDZ + s-,p-Rydberg)
!
memory,1000,m          ! for n processors we need to reserve 1000*10^6*8*n=8*n Gigabyte of
```

```
file,2,wavefunction.wfu,new   ! orbitals and wavefunctions are stored here


! Specify the number of electronic states, the total charge and spin (2*S)
Nst=9
set,charge=0
set,spin=1
! active space
nr_active_electrons=7
nr_active_orbitals=11


Nel=49-charge     ! number of electrons


nclosed=(Nel-nr_active_electrons)/2    ! orbitals up to nclosed are doubly occupied
nocc=nclosed+nr_active_orbitals        ! orbitals up to nocc can have non-zero occupation numbers
! aug-cc-pVDZ + s-,px-,py- and pz-Rydberg orbitals on atom 1
basis={
!
! HYDROGEN         (5s,2p) -> [3s,2p]
! HYDROGEN         (4s,1p) -> [2s,1p]
! HYDROGEN         (1s,1p)
s, H , 13.0100000, 1.9620000, 0.4446000, 0.1220000, 0.0297400
c, 1.3, 0.0196850, 0.1379770, 0.4781480
c, 4.4, 1
c, 5.5, 1
p, H , 0.7270000, 0.1410000
c, 1.1, 1
c, 2.2, 1
! CARBON          (10s,5p,2d) -> [4s,3p,2d]
! CARBON          (9s,4p,1d) -> [3s,2p,1d]
! CARBON          (1s,1p,1d)
s, C , 6665.0000000, 1000.0000000, 228.0000000, 64.7100000, 21.0600000, 7.4950000, 2.7970000, 0.5215000, 0.1596000, 0.0469000
c, 1.8, 0.0006920, 0.0053290, 0.0270770, 0.1017180, 0.2747400, 0.4485640, 0.2850740, 0.0152040
c, 1.8, -0.0001460, -0.0011540, -0.0057250, -0.0233120, -0.0639550, -0.1499810, -0.1272620, 0.5445290
c, 9.9, 1
c, 10.10, 1
p, C , 9.4390000, 2.0020000, 0.5456000, 0.1517000, 0.0404100
c, 1.3, 0.0381090, 0.2094800, 0.5085570
c, 4.4, 1
c, 5.5, 1
d, C , 0.5500000, 0.1510000
c, 1.1, 1
c, 2.2, 1
! CARBON          (10s,5p,2d) -> [4s,3p,2d]
! CARBON          (9s,4p,1d) -> [3s,2p,1d]
! CARBON          (1s,1p,1d)
s, C1 , 6665.0000000, 1000.0000000, 228.0000000, 64.7100000, 21.0600000, 7.4950000, 2.7970000, 0.5215000, 0.1596000, 0.0469000
c, 1.8, 0.0006920, 0.0053290, 0.0270770, 0.1017180, 0.2747400, 0.4485640, 0.2850740, 0.0152040
c, 1.8, -0.0001460, -0.0011540, -0.0057250, -0.0233120, -0.0639550, -0.1499810, -0.1272620, 0.5445290
c, 9.9, 1
c, 10.10, 1
p, C1 , 9.4390000, 2.0020000, 0.5456000, 0.1517000, 0.0404100
c, 1.3, 0.0381090, 0.2094800, 0.5085570
c, 4.4, 1
c, 5.5, 1
d, C1 , 0.5500000, 0.1510000
c, 1.1, 1
```

```
c, 2.2, 1
! s-Rydberg orbital on carbon C1, the exponents were generated using the script
! Kaufmann_exponents.py (Z=1, n=3, l=0), see reference therein
s, C1 , 0.02729391, 0.01094397, 0.00585838
c, 1.1, 1.0000000
c, 2.2, 1.0000000
c, 3.3, 1.0000000
! p-Rydberg orbitals on carbon C1, the exponents were generated using the script
! Kaufmann_exponents.py (Z=1, n=3, l=1), see reference therein
p, C1, 0.04778691, 0.01881568, 0.00998821
c, 1.1, 1.0000000
c, 2.2, 1.0000000
c, 3.3, 1.0000000
}
! records
orbrecAVDZ=2140.2   ! orbital record


! convergence thresholds
gthresh,gradient=1.d-5,energy=1.d-10     ! tighten threshold for energy convergence

symmetry,nosym
angstrom
geomtyp=xyz
orient,noorient        ! If the molecule is reoriented, the gradients point into the wrong direction

geometry={
    14
D0 ground state minimum, SA-5-CASSCF(7,8)/(6-31G*,s-Rydberg), ENERGY = -269.19211
  C1       -0.0000000103        0.0087622008        0.9222117206
  C         1.2180616537        0.0070686004        0.1797720304
  C         1.2124247003        0.0047926527       -1.2075691077
  C         0.0000000020        0.0045254951       -1.9151098967
  C        -1.2124247007        0.0047926658       -1.2075691120
  C        -1.2180616719        0.0070686096        0.1797720253
  C         0.0000000081        0.0118532327        2.3297334406
  H         2.1525796224        0.0077249136        0.7123445232
  H         2.1444293404        0.0035748978       -1.7440123152
  H         0.0000000007        0.0013194687       -2.9896399137
  H        -2.1444293347        0.0035749181       -1.7440123314
  H        -2.1525796424        0.0077249355        0.7123445070
  H        -0.9182582646        0.0136087018        2.8856031764
  H         0.9182582969        0.0136087074        2.8856031530
}


{hf
 orbital,orbrecAVDZ}


put,molden,hf_orbitals.avdz.molden;


! At the HF/(aug-cc-pVDZ + s-,p-Rydberg) level
!     pi1: 21
!     pi2: 23
!     pi3: 24
!     pi4: 25
!     s-Rydberg: 26
!     px-Rydberg: 27
```

```
!     pz-Rydberg: 28
!     py-Rydberg: 29
!     pi5*: 41
!     pi6*: 43 (?)
!     pi7*: 72


! swap orbitals so that the active space consists of
! all pi-orbitals (22.1-28.1) and the Rydberg orbitals (29.1-32.1)
{merge
 orbital,orbrecAVDZ;
 move;                 ! copy all input orbitals to the set of output orbitals
 rotate,21.1,22.1   ! exchange orbitals 21 and 22
 ! move Rydberg orbitals to positions 29.1-32.1
 rotate,29.1,32.1
 rotate,28.1,31.1
 rotate,27.1,30.1
 rotate,26.1,29.1
 ! move pi* orbitals to positions 26.1-28.1
 rotate,41.1,26.1
 rotate,43.1,27.1
 rotate,72.1,28.1
 save,orbrecAVDZ;
}


put,molden,hf_reordered.avdz.molden;


! CASSCF calcualation with AVDZ,Rydberg basis set
{multi; failsafe;
 closed,nclosed; occ,nocc;
 wf,Nel,1,spin;
 pspace,10.0;
 state,Nst;
 start,orbrecAVDZ; ! start with these orbitals
 save,orbrecAVDZ;
 tran,dm;          ! request transition dipoles
 dm;               ! save individual density matrices in AO basis
}


! save CASSCF excitation energies and CASSCF oscillator strengths
DO i=1,Nst
 ! compute oscillator strengths
 k=(i-1)*(i-2)/2+1
 f(i)=2.0/3.0*(TRDMX(k)**2 + TRDMY(k)**2 + TRDMZ(k)**2)
 ! compute excitation energies in eV
 enexc(i)=(ENERGY(i)-ENERGY(1))/EV
ENDDO


! save energies for each basis set to a different file
f(1)=0.0      ! no oscillator strength defined for ground state
{table,enexc,f
 heading,Exc.Energy/eV, Osc.Strength
 save,casscf_exc_energies.avdz.tab,new}
{table,ENERGY
 save,casscf_energies.avdz.tab,new}


! The optimized orbitals are sorted by their occupancy in the ground state:
```

```
!    22: pi1   (1.91)
!    23: pi2   (1.80)
!    24: pi3   (1.76)
!    25: pi4   (0.60)
!    26: pi5* (0.23)
!    27: pi6* (0.15)
!    28: s-Rydberg   (0.13)
!    29: px-Rydberg (0.12)
!    30: pz-Rydberg (0.12)
!    31: py-Rydberg (0.12)
!    32: pi7* (0.06)


{put,molden,mcscf_orbitals.avdz.molden;
 orbital,orbrecAVDZ;
}


! We will analyze the character of the (excited) states in terms of the diagonal
! elements of the single-particle density matrices of each state.
! For instance, pi1 is the the occupation of the totally bonding pi-orbital in the i-th state
DO i=1,Nst
    {matrop
    load,P,den,orbrecAVDZ,state=i,symmetry=1;     ! load density matrix for state i
    load,C,orb,orbrecAVDZ;                         ! load MO coefficients
    dmo,Pmo,P,C;                                   ! transform density matrix into MO basis
    ! assign diagonal matrix elements to variables, these are the occupations of
    ! the active orbitals
    ! ... occupied pi-orbitals
    elem,pi1,Pmo,22.1,22.1;
    elem,pi2,Pmo,23.1,23.1;
    elem,pi3,Pmo,24.1,24.1;
    elem,pi4,Pmo,25.1,25.1;
    ! ... virtual pi-orbitals
    elem,pi5s,Pmo,26.1,26.1;
    elem,pi6s,Pmo,27.1,27.1;
    elem,pi7s,Pmo,32.1,32.1;
    ! ... Rydberg orbitals
    elem,sRyd,Pmo,28.1,28.1;    ! in the optimized MOs the Rydberg orbitals have higher occupation than the pi7* orbital
    elem,pxRyd,Pmo,29.1,29.1;
    elem,pzRyd,Pmo,30.1,30.1;
    elem,pyRyd,Pmo,31.1,31.1;
}
    ! save occupation numbers in each state
    {table,i,pi1,pi2,pi3,pi4,pi5s,pi6s,pi7s,sRyd,pxRyd,pzRyd,pyRyd
     heading,states,occ(pi1),occ(pi2),occ(pi3),occ(pi4),occ(pi5s),occ(pi6s),occ(pi7s),occ(sRyd),occ(pxRyd),occ(pzRyd),occ(PyRyd)
     save,dens_diag_occ.avdz.tab}


ENDDO


! Multireference configuration interaction
{mrci,swap;
 core,nclosed; closed,nclosed; occ, nocc;
 wf,Nel,1,spin;
 state,Nst;
 print,CI=0;
}
```

```
! save MRCI excitation energies and MRCI oscillator strengths
DO i=1,Nst
 ! compute oscillator strengths
 k=(i-1)*(i-2)/2+1
 f(i)=2.0/3.0*(TRDMX(k)**2 + TRDMY(k)**2 + TRDMZ(k)**2)
 ! compute excitation energies in eV
 enexc(i)=(ENERGD(i)-ENERGD(1))/EV
ENDDO

! save energies for each basis set to a different file
f(1)=0.0      ! no oscillator strength defined for ground state
{table,enexc,f
 heading,Exc.Energy/eV, Osc.Strength
 save,mrci_exc_energies.avdz.tab,new}
{table,ENERGD,ENERGP
 save,mrci_energies.avdz.tab,new}

EXIT
```

6 Key Geometries

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D0 ground state minimum, SA-5-CASSCF(7,8)/(6-31G*,s-Rydberg), ENERGY = -269.19211

C	-0.0000000103	0.0087622008	0.9222117206
C	1.2180616537	0.0070686004	0.1797720304
C	1.2124247003	0.0047926527	-1.2075691077
C	0.0000000020	0.0045254951	-1.9151098967
C	-1.2124247007	0.0047926658	-1.2075691120
C	-1.2180616719	0.0070686096	0.1797720253
C	0.0000000081	0.0118532327	2.3297334406
H	2.1525796224	0.0077249136	0.7123445232
H	2.1444293404	0.0035748978	-1.7440123152
H	0.0000000007	0.0013194687	-2.9896399137
H	-2.1444293347	0.0035749181	-1.7440123314
H	-2.1525796424	0.0077249355	0.7123445070
H	-0.9182582646	0.0136087018	2.8856031764

```
H           0.9182582969           0.0136087074           2.8856031530


    14

D3 metastable minimum, SA-5-CASSCF(7,8)/(6-31G*,s-Rydberg), ENERGY = -269.085999
 C          -0.0000000031           0.0088067582           0.9056482017
 C           1.2381046432           0.0073617148           0.1830357725
 C           1.2290831643           0.0047535481          -1.1886861418
 C          -0.0000000043           0.0036812701          -1.8667907641
 C          -1.2290831702           0.0047535602          -1.1886861410
 C          -1.2381046499           0.0073617241           0.1830357769
 C           0.0000000078           0.0116338529           2.2738912336
 H           2.1596855257           0.0083319731           0.7306772596
 H           2.1459312125           0.0037295763          -1.7433173820
 H           0.0000000026           0.0013599317          -2.9411720221
 H          -2.1459312181           0.0037295970          -1.7433173809
 H          -2.1596855340           0.0083319908           0.7306772600
 H          -0.9160198245           0.0130822547           2.8322381202
 H           0.9160198481           0.0130822481           2.8322381072


    14

MECI(D4/D3), SA-5-CASSCF(7,8)/(6-31G*,s-Rydberg), ENERGY = -269.01904
 C      0.000000      0.010281      0.937650
 C      1.220124      0.008777      0.211613
 C      1.229653      0.007406     -1.244921
 C     -0.000000      0.000212     -1.966515
 C     -1.229653      0.007406     -1.244921
 C     -1.220124      0.008777      0.211613
```

```
C       0.000000      0.011233       2.360630

H       2.154325      0.008565       0.740315

H       2.166335      0.004838      -1.767360

H      -0.000000     -0.003422      -3.039449

H      -2.166335      0.004838      -1.767360

H      -2.154325      0.008565       0.740315

H      -0.919022      0.011263       2.913931

H       0.919022      0.011262       2.913931
```

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```

MECI(D3/D2), SA-5-CASSCF(7,8)/(6-31G*,s-Rydberg), ENERGY = -268.98964

```
C        0.0000000275      0.0087092947       0.8042062433

C        1.2192841617      0.0073994387       0.1407073140

C        1.2446995153      0.0049255783      -1.1102200914

C        0.0000000573      0.0036398215      -1.7729745984

C       -1.2446995839      0.0049247905      -1.1102200826

C       -1.2192843693      0.0074002149       0.1407072058

C        0.0000000777      0.0115037385       2.1958517545

H        2.1219058294      0.0085338058       0.7123727373

H        2.1452754046      0.0038247673      -1.6824329310

H        0.0000000803      0.0015586030      -2.8424839307

H       -2.1452753903      0.0038221577      -1.6824330526

H       -2.1219060193      0.0085363757       0.7123726479

H       -0.9096643177      0.0126107734       2.7470093847

H        0.9096645268      0.0126106400       2.7470092991
```

```
   14
```

```
MECI(D2/D1), SA-5-CASSCF(7,8)/(6-31G*,s-Rydberg), ENERGY = -269.08050
  C        -0.0000000059        0.0088106060        0.9536957257
  C         1.2442551832        0.0071212403        0.1857484899
  C         1.2303536595        0.0044008949       -1.2210428883
  C         0.0000000056        0.0032987226       -1.9369866465
  C        -1.2303536552        0.0044009399       -1.2210428931
  C        -1.2442551853        0.0071212847        0.1857484853
  C        -0.0000000057        0.0117928599        2.3464006104
  H         2.1787619701        0.0085720607        0.7152958720
  H         2.1596866778        0.0039191646       -1.7598373408
  H         0.0000000067        0.0013878095       -3.0102606488
  H        -2.1596866699        0.0039192407       -1.7598373511
  H        -2.1787619771        0.0085721358        0.7152958604
  H        -0.9179619161        0.0133415368        2.9031473187
  H         0.9179619123        0.0133415038        2.9031473062
```

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