Electronic Supplementary Material (ESI) for RSC Advances.

The *cis*- and *trans*-Formylperoxy Radical: Fundamental Vibrational Frequencies and Relative Energies of the $\tilde{\mathrm{X}}\,^2\mathrm{A}''$ and $\tilde{\mathrm{A}}\,^2\mathrm{A}'$ States

- Supplementary Information -

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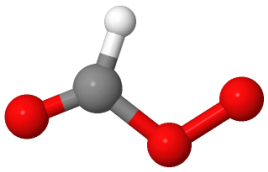
1.1 $\tilde{X}\ ^2A''$ *trans* formylperoxy radical HC(O)OO·

1.1.1 CCSD(T)/cc-pVQZ Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/PVQZ
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

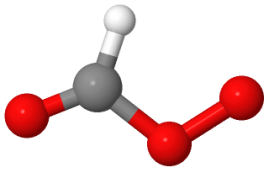
Equilibrium Geometry (Å):

H	-0.248436	1.408905	0.000000
C	-0.595896	0.370492	0.000000
O	0.516935	-0.505752	0.000000
O	1.639450	0.205389	0.000000
O	-1.693667	-0.066368	-0.000000

Harmonic Frequencies (cm-1):

3090.3840	1145.9039	605.0288
1871.8403	1016.2076	416.0285
1335.5966	1016.1118	172.4066

1.1.2 CCSD(T)/ANO2 Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

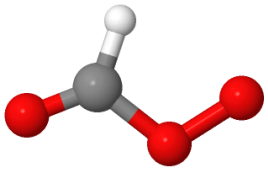
Equilibrium Geometry (Å):

H	-0.249412	1.409394	0.000000
C	-0.596061	0.371408	0.000000
O	0.516438	-0.505648	0.000000
O	1.640353	0.204985	0.000000
O	-1.693888	-0.066785	-0.000000

Harmonic Frequencies (cm-1):

3099.2524	1144.4528	603.7034
1866.3923	1016.1997	414.2455
1332.9326	1013.5329	171.1384

1.1.3 CCSD(T)/ANO1 Optimization and Harmonic Frequency



Program: CFOUR 2.0
Theory: CCSD(T)/ANO1
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

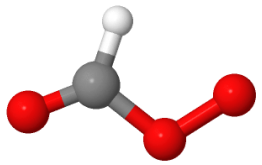
Equilibrium Geometry (Å):

H	-0.247859	1.409408	0.000000
C	-0.595999	0.370877	0.000000
O	0.516062	-0.508176	0.000000
O	1.644591	0.206346	0.000000
O	-1.697894	-0.065222	-0.000000

Harmonic Frequencies (cm-1):

3097.5917	1131.3149	604.0052
1864.1461	1019.8824	413.3251
1335.0990	1013.2208	170.5961

1.1.4 BCCSD(T)/ANO1 Optimization and Harmonic Frequency



Jmol

Program: PSI4
Theory: bccd(t)/ano1
Reference: uhf
Charge/Multiplicity: 0/2
Frozen Core: ON

SCF Convergence: 11
CC Convergence: 9
Brueckner Convergence: 8

Equilibrium Geometry (Å):

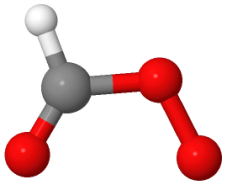
H	-0.247662	1.409379	0.000000
C	-0.596194	0.370870	0.000000
O	0.516022	-0.508584	0.000000
O	1.645017	0.206705	0.000000
O	-1.698147	-0.065165	0.000000

Harmonic Frequencies (cm-1):

170.390	1012.853	1333.981
412.777	1018.792	1864.380
603.243	1126.230	3096.471

1.2 $\tilde{X}\ ^2A''$ *cis* formylperoxy radical HC(O)OO·

1.2.1 CCSD(T)/cc-pVQZ Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/PVQZ
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

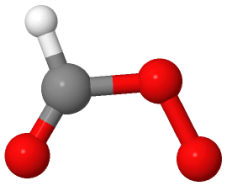
Equilibrium Geometry (Å):

```
H  -1.123944   1.520533  -0.000000
C  -0.734238   0.498638  -0.000000
O   0.676699   0.615414  -0.000000
O   1.280149  -0.567113   0.000000
O  -1.335176  -0.518207   0.000000
```

Harmonic Frequencies (cm-1):

```
3099.1641  1109.1334  800.6800
1864.7082  987.6379  335.1518
1373.7218  908.0123  239.0331
```

1.2.2 CCSD(T)/ANO2 Optimization and Harmonic Frequency



Program: CFOUR 2.0
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

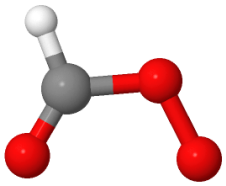
Equilibrium Geometry (Å):

H	-1.124612	1.520292	-0.000000
C	-0.734857	0.498982	-0.000000
O	0.676557	0.615768	-0.000000
O	1.280770	-0.567156	0.000000
O	-1.335148	-0.518760	0.000000

Harmonic Frequencies (cm-1):

3107.0739	1109.0286	799.6646
1859.9000	985.6385	334.9625
1373.0343	905.7961	238.1553

1.2.3 CCSD(T)/ANO1 Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/ANO1
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

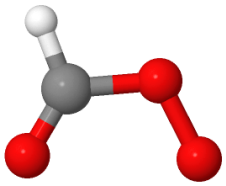
Equilibrium Geometry (Å):

```
H  -1.125523   1.521861  -0.000000
C  -0.735087   0.499636  -0.000000
O   0.676564   0.619047  -0.000000
O   1.283948  -0.569629   0.000000
O  -1.338104  -0.520155   0.000000
```

Harmonic Frequencies (cm-1):

```
3104.8305  1096.5547  799.4175
1857.6036  985.9039  334.2769
1374.1775  909.3925  238.0211
```

1.2.4 BCCSD(T)/ANO1 Optimization and Harmonic Frequency



Jmol

Program: PSI4
Theory: bccd(t)/ano1
Reference: uhf
Charge/Multiplicity: 0/2
Frozen Core: ON

SCF Convergence: 11
CC Convergence: 9
Brueckner Convergence: 8

Equilibrium Geometry (Å):

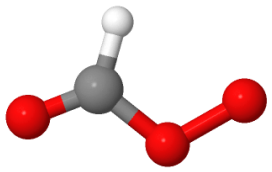
```
H  -1.125743   1.522032   0.000000
C  -0.735362   0.499681   0.000000
O   0.676747   0.619321   0.000000
O   1.284129  -0.569907   0.000000
O  -1.338247  -0.520195   0.000000
```

Harmonic Frequencies (cm-1):

```
238.177  907.794  1373.109
333.896  985.280  1858.204
798.421  1094.416  3103.723
```

1.3 $\tilde{A}\ ^2A'$ *trans* formylperoxy radical HC(O)OO·

1.3.1 CCSD(T)/cc-pVQZ Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/PVQZ
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

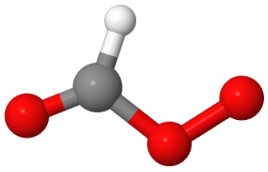
Equilibrium Geometry (Å):

```
H  -0.299215   1.421880   0.000000
C  -0.599299   0.371193   0.000000
O   0.482159  -0.491499   0.000000
O   1.689121   0.188934   0.000000
O  -1.702809  -0.065509  -0.000000
```

Harmonic Frequencies (cm-1):

```
3098.7562  1056.1858  600.5472
1838.2260  1009.0379  334.4929
1397.3252  958.5580  192.8654
```

1.3.2 CCSD(T)/ANO2 Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

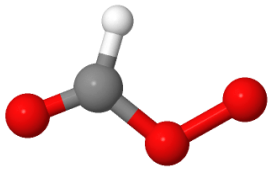
Equilibrium Geometry (Å):

```
H  -0.300248   1.422244   0.000000
C  -0.599828   0.372179   0.000000
O   0.482004  -0.491182   0.000000
O   1.690144   0.188463   0.000000
O  -1.703215  -0.066118  -0.000000
```

Harmonic Frequencies (cm-1):

```
3108.2874  1054.2317  599.0305
1832.6446  1007.7757  333.3108
1395.0312  957.4096  192.3133
```

1.3.3 CCSD(T)/ANO1 Optimization and Harmonic Frequency



Program: CFOUR 2.0
Theory: CCSD(T)/ANO1
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

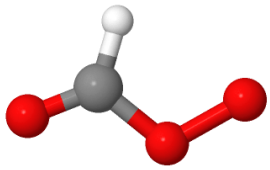
Equilibrium Geometry (Å):

H	-0.297534	1.422256	0.000000
C	-0.599646	0.371714	0.000000
O	0.480929	-0.495233	0.000000
O	1.694955	0.190595	0.000000
O	-1.707260	-0.063852	-0.000000

Harmonic Frequencies (cm-1):

3104.9912	1059.3585	598.0344
1832.1421	1006.5647	332.1412
1398.4337	945.9744	190.7914

1.3.4 BCCSD(T)/ANO1 Optimization and Harmonic Frequency



Program: PSI4
Theory: bccd(t)/ano1
Reference: uhf
Charge/Multiplicity: 0/2
Frozen Core: ON

SCF Convergence: 11
CC Convergence: 9
Brueckner Convergence: 8

Equilibrium Geometry (Å):

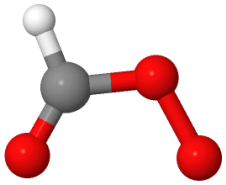
H	-0.298281	1.422743	0.000000
C	-0.600504	0.372225	0.000000
O	0.481366	-0.494705	0.000000
O	1.695768	0.189829	0.000000
O	-1.707818	-0.064027	0.000000

Harmonic Frequencies (cm-1):

190.920	939.334	1396.527
331.816	1005.601	1832.160
596.350	1055.397	3104.827

1.4 $\tilde{A}\ ^2A'$ *cis* formylperoxy radical HC(O)OO·

1.4.1 CCSD(T)/cc-pVQZ Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/PVQZ
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

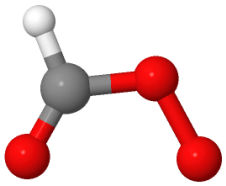
Equilibrium Geometry (Å):

```
H  -1.137073   1.507955  -0.000000
C  -0.725841   0.494721  -0.000000
O   0.636310   0.644639  -0.000000
O   1.294097  -0.572244   0.000000
O  -1.314207  -0.538569   0.000000
```

Harmonic Frequencies (cm-1):

```
3100.4966  1064.5793  773.9152
1819.8427  1013.8595  374.9347
1380.5959  896.3374  254.7769
```

1.4.2 CCSD(T)/ANO2 Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

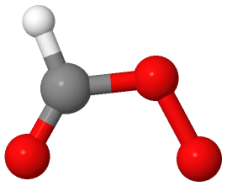
Equilibrium Geometry (Å):

```
H  -1.137559   1.507840  -0.000000
C  -0.726358   0.495170  -0.000000
O   0.636325   0.644908  -0.000000
O   1.294301  -0.572347   0.000000
O  -1.314008  -0.539063   0.000000
```

Harmonic Frequencies (cm-1):

```
3108.1655  1062.6637  772.7909
1814.5482  1012.4266  375.3528
1379.7004  895.1643  254.8197
```

1.4.3 CCSD(T)/ANO1 Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/ANO1
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

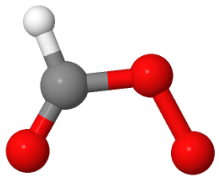
Equilibrium Geometry (Å):

```
H  -1.140163   1.509056  -0.000000
C  -0.727437   0.495755  -0.000000
O   0.636335   0.649634  -0.000000
O   1.297392  -0.575498   0.000000
O  -1.316135  -0.541154   0.000000
```

Harmonic Frequencies (cm-1):

```
3105.3477  1065.4968  773.3458
1815.6999  1011.7611  372.2137
1380.6727  883.3870  254.1774
```

1.4.4 BCCSD(T)/ANO1 Optimization and Harmonic Frequency



Jmol

Program: PSI4
Theory: bccd(t)/ano1
Reference: uhf
Charge/Multiplicity: 0/2
Frozen Core: ON

SCF Convergence: 11
CC Convergence: 9
Brueckner Convergence: 8

Equilibrium Geometry (Å):

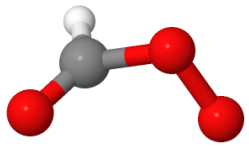
H	-1.139746	1.509340	0.000000
C	-0.728197	0.495490	0.000000
O	0.636615	0.649113	0.000000
O	1.298949	-0.574920	0.000000
O	-1.317429	-0.541032	0.000000

Harmonic Frequencies (cm-1):

253.338	878.241	1379.421
372.235	1010.759	1816.226
771.543	1059.389	3104.503

1.5 Formylperoxy radical isomerization transition state HC(O)OO·

1.5.1 CCSD(T)/cc-pVQZ Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/PVQZ
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

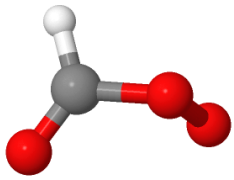
Equilibrium Geometry (Å):

```
H  -0.774922   1.005152  -1.182867
C  -0.666276   0.357088  -0.309239
O   0.630714   0.535369   0.285457
O   1.382478  -0.484455  -0.126980
O  -1.464499  -0.382149   0.148057
```

Harmonic Frequencies (cm-1):

```
3099.3151  1139.9929  621.4357
1855.5617  1033.2645  316.5397
1353.3045  907.7879  233.1685i
```

1.5.2 CCSD(T)/ANO2 Optimization and Harmonic Frequency



Jmol

Program: CFOUR 2.0
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: UHF
Frozen Core: ON

SCF Convergence: 9
CC Convergence: 9
Geometry Convergence: 9
Lineq Convergence: 7
Integral Thresh: 0.10E-13

Equilibrium Geometry (Å):

```
H  -0.775019   1.005190  -1.182839
C  -0.666785   0.357566  -0.309649
O   0.630523   0.535604   0.285802
O   1.382972  -0.484547  -0.127155
O  -1.464413  -0.382653   0.148193
```

Harmonic Frequencies (cm-1):

```
3108.3425  1139.3904  620.5159
1850.9331  1031.8925  315.6823
1352.2383  906.4580  233.1203i
```

2 Treatment of Fermi Resonance

Fermi resonances, in this work, were treated with the standard procedure provided by Nielson.[1] This method modifies the VPT2 treatment, in instances when $\nu_r \approx \nu_s + \nu_t$, by computing a replacement term for the anharmonic constant x_{rs}. Rather than eliminate the cubic force field terms from the first-order Hamiltonian by performing a contact transformation on the (ν_r, $\nu_s + \nu_t$) interaction, the correction becomes

$$\frac{\phi_{rst}^2 \nu_r (\nu_r^2 - \nu_s^2 - \nu_t^2)}{(\nu_r + \nu_s + \nu_t)(\nu_r + \nu_s - \nu_t)(\nu_r - \nu_s + \nu_t)(\nu_r - \nu_s - \nu_t)}$$

$$\rightarrow \frac{1}{4}\left[\frac{1}{(\nu_r + \nu_s + \nu_t)} + \frac{1}{(\nu_r - \nu_s + \nu_t)} + \frac{1}{(\nu_r + \nu_s - \nu_t)}\right]$$

Next, the first-order Hamiltonian's remaining resonance interaction is treated by explicitly diagonalizing the 2×2 matrix

$$\begin{bmatrix} \nu_r & \frac{\phi_{rst}}{\sqrt{8}} \\ \frac{\phi_{rst}}{\sqrt{8}} & \nu_s + \nu_t \end{bmatrix}$$

where the matrix element of the anharmonic potential across the zeroth-order, quasidegenerate states (ν_r and $\nu_s + \nu_t$) is most affected by the off-diagonal element of the cubic force constant ϕ_{rst}. A cutoff of ($\phi \geq 80$ cm^{-1} and $\delta \leq 50$ cm^{-1}) prevents exclusion of any interactions other than the (ν_2, $\nu_5 + \nu_5$), which occurred only in the *cis*-$\tilde{\mathrm{X}}\,^2\mathrm{A}''$ isomer. The potential resonances of (ν_8, $\nu_9 + \nu_6$) in the *cis*, and (ν_3, $\nu_8 + \nu_9$) in the *trans* required lowering the threshold to $\phi \geq 50$ and 26 cm^{-1} respectively.

References

[1] H. H. Nielsen. The Vibrational-Rotation Energies of Molecules. *Rev. Mod. Phys.*, 23(90):90–136, 1951.