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

Ethylperoxy radical: approaching spectroscopic accuracy via coupled-cluster theory

- Supplementary material -

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Contents

1 $\tilde{\mathrm{X}}\ ^2\mathrm{A}''$ *trans*-ethylperoxy radical - *trans*-$\mathrm{C_2H_5O_2}$

Program: MOLPRO 2010.1
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: ROHF
Frozen core: True
Point group: C_s

SCF energy convergence: 10^{-11}
CC energy convergence: 10^{-11}
CC amplitudes convergence: 10^{-10}
Geometry convergence: 10^{-7}
Integral threshold: 10^{-14}

CCSD/ANO2 max. $|t_{ij}^{ab}|$: 0.02

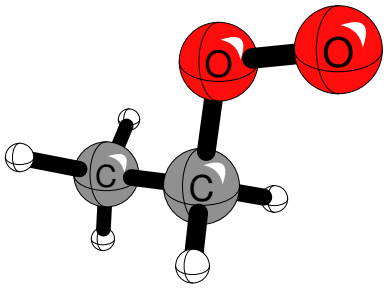
CASSCF(13, 13)/ANO2 C_0: 0.959

Equilibrium geometry (Å):

C	-0.5188089230	0.5519246235	0.0000000000
O	0.5195698892	-0.4634981016	0.0000000000
O	1.7128897373	0.0970022242	0.0000000000
H	-0.3719869679	1.1634044573	-0.8895952302
H	-0.3719869679	1.1634044573	0.8895952302
C	-1.8448044293	-0.1715485927	0.0000000000
H	-1.9440500120	-0.7983462147	-0.8857571760
H	-1.9440500120	-0.7983462147	0.8857571760
H	-2.6555411064	0.5573668140	0.0000000000

Harmonic frequencies (cm^{-1}):

a' modes	a'' modes
3136	3148
3076	3126
3053	1494
1517	1283
1506	1162
1424	806
1383	231
1185	89
1148	
1046	
866	
507	
309	



2 $\tilde{X}\ ^2A$ *gauche*-ethylperoxy radical - *gauche*-$C_2H_5O_2$

Program: MOLPRO 2010.1
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: ROHF
Frozen core: True
Point group: C_1

SCF energy convergence: 10^{-11}
CC energy convergence: 10^{-11}
CC amplitudes convergence: 10^{-10}
Geometry convergence: 10^{-7}
Integral threshold: 10^{-14}

CCSD/ANO2 max. $|t_{ij}^{ab}|$: 0.02

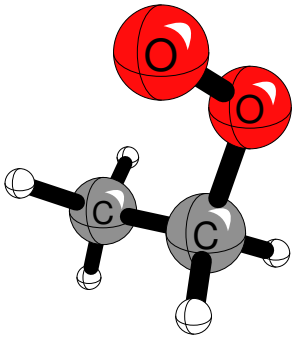
CASSCF(13, 13)/ANO2 C_0: 0.961

Equilibrium geometry (Å):

C	-1.5324940327	0.5216233876	0.1228005797
C	-0.6143783090	-0.5976590595	-0.3137263631
H	-1.6851097546	0.4962878490	1.2016466808
H	-2.5004651000	0.4144612538	-0.3686383853
H	-1.1045663144	1.4842005737	-0.1536382651
O	0.6771826255	-0.4875361609	0.3412337902
H	-0.4308936246	-0.5895727155	-1.3872607330
H	-0.9777114159	-1.5774385541	-0.0053476245
O	1.3555617142	0.5302222814	-0.1530519220

Harmonic frequencies (cm^{-1}):

a modes	a modes (cont.)
3153	1205
3135	1160
3129	1110
3079	1018
3051	866
1511	802
1494	531
1490	363
1413	234
1383	125
1312	



3 $\tilde{A}\ ^2A'$ *trans*-ethylperoxy radical - *trans*-$C_2H_5O_2$

Program: MOLPRO 2010.1
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: ROHF
Frozen core: True
Point group: C_s

SCF energy convergence: 10^{-11}
CC energy convergence: 10^{-11}
CC amplitudes convergence: 10^{-10}
Geometry convergence: 10^{-7}
Integral threshold: 10^{-14}

CCSD/ANO2 max. $|t_{ij}^{ab}|$: 0.02

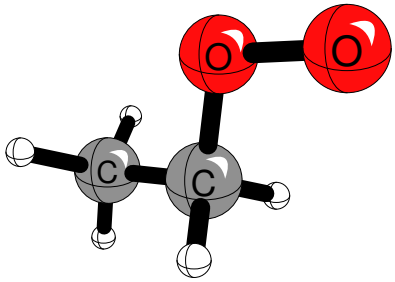
CASSCF(13, 13)/ANO2 C_0: 0.963

Equilibrium geometry (Å):

C	-0.4956885719	0.5430564253	0.0000000000
O	0.4858949109	-0.5108647141	0.0000000000
O	1.7242024334	0.1244981797	0.0000000000
H	-0.3510151994	1.1579201425	-0.8912164899
H	-0.3510151994	1.1579201425	0.8912164899
C	-1.8420084989	-0.1447691015	0.0000000000
H	-1.9545447709	-0.7674520567	-0.8865786907
H	-1.9545447709	-0.7674520567	0.8865786907
H	-2.6301702073	0.6086421759	0.0000000000

Harmonic frequencies (cm^{-1}):

a' modes	a'' modes
3137	3146
3055	3091
3044	1490
1535	1284
1510	1192
1420	835
1391	236
1135	141
1052	
982	
866	
437	
286	



4 $\tilde{A}\ ^2A$ *gauche*-ethylperoxy radical - *gauche*-$C_2H_5O_2$

Program: MOLPRO 2010.1
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: ROHF
Frozen core: True
Point group: C_1

SCF energy convergence: 10^{-11}
CC energy convergence: 10^{-11}
CC amplitudes convergence: 10^{-10}
Geometry convergence: 10^{-7}
Integral threshold: 10^{-14}

CCSD/ANO2 max. $|t_{ij}^{ab}|$: 0.02

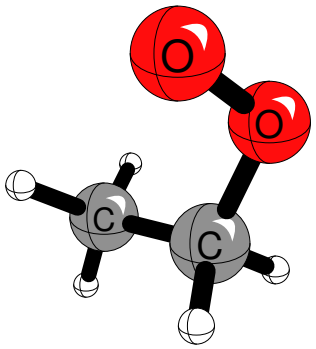
CASSCF(13, 13)/ANO2 C_0: 0.955

Equilibrium geometry (Å):

```
C   0.1464604158  -0.5367025185  -1.5160893616
C  -0.3244778801   0.5832145568  -0.6104005954
H   1.2299209247  -0.5061553528  -1.6267460923
H  -0.3096873161  -0.4204070726  -2.5008003884
H  -0.1368517924  -1.5098957044  -1.1180395184
O   0.3164337434   0.5619703322   0.6808322459
H  -1.4064302258   0.5620822257  -0.4605196798
H  -0.0393765366   1.5620908218  -0.9933453042
O  -0.1411298020  -0.5771854991   1.3366659546
```

Harmonic frequencies (cm^{-1}):

a modes	a modes (cont.)
3149	1182
3130	1115
3124	1048
3056	946
3050	859
1511	803
1496	460
1490	339
1419	231
1388	131
1314	



5 $\tilde{X}\ ^2A''$ methylperoxy radical - CH_3O_2

Program: MOLPRO 2010.1
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: ROHF
Frozen core: True
Point group: C_s

SCF energy convergence: 10^{-11}
CC energy convergence: 10^{-11}
CC amplitudes convergence: 10^{-10}
Geometry convergence: 10^{-7}
Integral threshold: 10^{-14}

CCSD/ANO2 max. $|t_{ij}^{ab}|$: 0.03

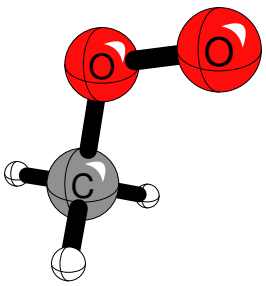
CASSCF(19, 15)/ANO2 C_0: 0.957

Equilibrium geometry (Å):

O	-0.0534713074	0.5312873379	0.0000000000
O	-1.0962381809	-0.2767259455	0.0000000000
C	1.1661274192	-0.2372916157	0.0000000000
H	1.9715584512	0.4930692692	0.0000000000
H	1.1951430248	-0.8538763414	-0.8954041101
H	1.1951430248	-0.8538763414	0.8954041101

Harmonic frequencies (cm^{-1}):

a' modes	a'' modes
3175	3165
3064	1484
1497	1146
1450	155
1218	
1166	
948	
495	



6 $\tilde{A}\ ^2A'$ methylperoxy radical - CH_3O_2

Program: MOLPRO 2010.1
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: ROHF
Frozen core: True
Point group: C_s

SCF energy convergence: 10^{-11}
CC energy convergence: 10^{-11}
CC amplitudes convergence: 10^{-10}
Geometry convergence: 10^{-7}
Integral threshold: 10^{-14}

CCSD/ANO2 max. $|t_{ij}^{ab}|$: 0.03

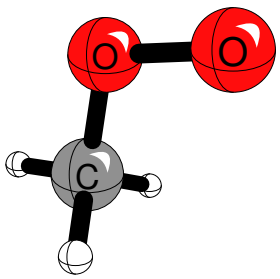
CASSCF(19, 15)/ANO2 C_0: 0.959

Equilibrium geometry (Å):

O	-0.0149524153	0.5777485552	0.0000000000
O	-1.1072340140	-0.2873804332	0.0000000000
C	1.1363598135	-0.2721046276	0.0000000000
H	1.9770314586	0.4166263109	0.0000000000
H	1.1512199521	-0.8925379689	-0.8967962411
H	1.1512199521	-0.8925379689	0.8967962411

Harmonic frequencies (cm^{-1}):

a' modes	a'' modes
3168	3122
3041	1478
1519	1177
1455	251
1185	
1037	
913	
385	



7 $\tilde{\mathrm{X}}\ ^2\mathrm{A}''$ hydroperoxy radical - $\mathrm{HO_2}$

Program: MOLPRO 2010.1
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: ROHF
Frozen core: True
Point group: C_s

SCF energy convergence: 10^{-11}
CC energy convergence: 10^{-11}
CC amplitudes convergence: 10^{-10}
Geometry convergence: 10^{-7}
Integral threshold: 10^{-14}

CCSD/ANO2 max. $|t_{ij}^{ab}|$: 0.04

CASSCF(13, 9)/ANO2 C_0: 0.974

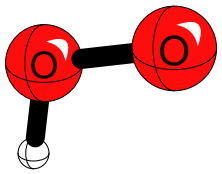
Equilibrium geometry (Å):

```
O  -0.6937342972   0.0081785728   0.0000000000
O   0.6354757377  -0.0626608366   0.0000000000
H   0.9246056151   0.8646730647   0.0000000000
```

Harmonic frequencies (cm^{-1}):

a' modes

```
3666
1439
1140
```



8 $\tilde{A}\ ^2A'$ hydroperoxy radical - HO_2

Program: MOLPRO 2010.1
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: ROHF
Frozen core: True
Point group: C_s

SCF energy convergence: 10^{-11}
CC energy convergence: 10^{-11}
CC amplitudes convergence: 10^{-10}
Geometry convergence: 10^{-7}
Integral threshold: 10^{-14}

CCSD/ANO2 max. $|t_{ij}^{ab}|$: 0.05

CASSCF(13, 9)/ANO2 C_0: 0.975

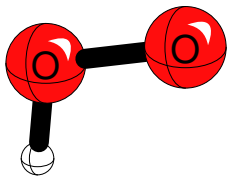
Equilibrium geometry (Å):

```
O  -0.7274772623   0.0053963302   0.0000000000
O   0.6699666871  -0.0606912331   0.0000000000
H   0.9127345618   0.8775702371   0.0000000000
```

Harmonic frequencies (cm^{-1}):

a' modes

```
3748
1231
 957
```



9 $\tilde{\mathrm{X}}\ ^2\mathrm{A}_2''$ methyl radical - $\mathrm{CH_3}$

Program: MOLPRO 2010.1
Theory: CCSD(T)/ANO2
Charge/Multiplicity: 0/2
Reference: ROHF
Frozen core: True
Point group: D_{3h}

SCF energy convergence: 10^{-11}
CC energy convergence: 10^{-11}
CC amplitudes convergence: 10^{-10}
Geometry convergence: 10^{-7}
Integral threshold: 10^{-14}

CCSD/ANO2 max. $|t_{ij}^{ab}|$: 0.04

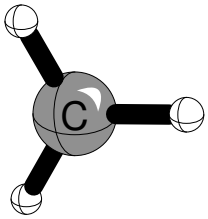
CASSCF(12, 12)/ANO2 C_0: 0.983

Equilibrium geometry (Å):

```
C  0.0000000000  0.0000000000  0.0000005123
H  0.0000000000  0.0000000000 -1.0779420065
H  0.0000000000 -0.9335253407  0.5389679533
H -0.0000000000  0.9335253407  0.5389679533
```

Harmonic frequencies (cm^{-1}):

a_1' modes	a_2'' modes	e modes
3120	507	3306
		1421



10 Incremented focal point tables for RO_2 $\tilde{A} \leftarrow \tilde{X}$ T_0 values (R = CH_3, H)

TABLE S-I. Incremented focal point table for $\tilde{A} \leftarrow \tilde{X}$ transition origins (T_0) for the CH_3O_2 and HO_2 systems. See Sec. II of the main paper for nuances of the different theoretical methods, extrapolation schemes, and corrections. All unlabeled values are in cm^{-1}.

A. $\tilde{A}\ ^2A'$ CH_3O_2 relative to $\tilde{X}\ ^2A''$ CH_3O_2.							
Basis set	ΔE_e[ROHF]	$+\delta$[RMP2]	$+\delta$[CCSD]	$+\delta$[CCSD(T)]	$+\delta$[CCSDT]	$+\delta$[CCSDT(Q)/B]	ΔE_e[CCSDT(Q)/B]
ANO0[a]	+4251	+2279	+70	+203	+19	+28	[+6850]
cc-pVTZ	+4483	+2289	+173	+280	[+19]	[+28]	[+7273]
cc-pVQZ	+4522	+2338	+201	+304	[+19]	[+28]	[+7411]
cc-pV5Z	+4522	+2350	+212	+315	[+19]	[+28]	[+7445]
CBS limit	[+4518]	[+2362]	[+223]	[+326]	[+19]	[+28]	**[+7476]**
$T_0 = \Delta E_e + \Delta_{ZPVE} + \Delta_{core} + \Delta_{rel}$							
$= 7476 - 115 + 22 - 7 =$ **7376 cm^{-1} (21.09 kcal mol^{-1})**							
B. $\tilde{A}\ ^2A'$ HO_2 relative to $\tilde{X}\ ^2A''$ HO_2.							
ANO0[a]	+4508	+1908	–40	+165	+16	+19	[+6577]
cc-pVTZ	+4762	+1949	+41	+231	[+16]	[+19]	[+7018]
cc-pVQZ	+4796	+1989	+63	+249	[+16]	[+19]	[+7132]
cc-pV5Z	+4795	+1993	+70	+257	[+16]	[+19]	[+7149]
CBS limit	[+4789]	[+1996]	[+77]	[+265]	[+16]	[+19]	**[+7162]**
$T_0 = 7162 - 155 + 10 - 7 =$ **7011 cm^{-1} (20.05 kcal mol^{-1})**							

[a]Utilized in computation of additive corrections for higher order excitations (no contribution to extrapolation scheme).

11 Harmonic vibrational frequency assignments for $\tilde{A}\ ^2A'$ *trans*- and $\tilde{A}\ ^2A$ *gauche*-$C_2H_5O_2$

TABLE S-II. CCSD(T)/ANO2 predictions for harmonic vibrational frequencies (ω) of $\tilde{A}\ ^2A'$ *trans*- and $\tilde{A}\ ^2A$ *gauche*-$C_2H_5O_2$. All values are in cm^{-1}.

Mode	Description	Symmetry[a]	*trans*-$C_2H_5O_2$	*gauche*-$C_2H_5O_2$
ω_1	CH_3 antisym. str.	a'	3137	3130
ω_2	CH_3 sym. str.	a'	3055	3050
ω_3	CH_2 sym. str.	a'	3044	3056
ω_4	CH_3/CH_2 scissor	a'	1535	1511
ω_5	CH_3/CH_2 scissor	a'	1510	1496
ω_6	CH_3 umbrella	a'	1420	1419
ω_7	CH_2 wag	a'	1391	1388
ω_8	CH_3 rock	a'	1135	1115
ω_9	CC str.	a'	1052	1048
ω_{10}	OO str.	a'	982	946
ω_{11}	CO str.	a'	866	859
ω_{12}	COO bend	a'	437	460
ω_{13}	CCO bend	a'	286	339
ω_{14}	CH_3/CH_2 antisym. str.	a''	3146	3149
ω_{15}	CH_3/CH_2 antisym. str.	a''	3091	3124
ω_{16}	CH_3 deform.	a''	1490	1490
ω_{17}	CH_2 twist	a''	1284	1314
ω_{18}	CH_2 twist	a''	1192	1182
ω_{19}	CH_3/CH_2 antisym. rock	a''	835	803
ω_{20}	CH_3 torsion	a''	236	231
ω_{21}	CCOO torsion	a''	141	131

[a]In the case of *gauche*-$C_2H_5O_2$, the symmetry labels correlate with the symmetry of the analogous mode in *trans*-$C_2H_5O_2$. As the *gauche* conformer possesses C_1 symmetry, its normal modes are rigorously of a symmetry.

12 Fermi type 2 resonance calculations for $\tilde{\mathrm{X}}\ ^2\mathrm{A}''$ *trans*-$\mathrm{C_2H_5O_2}$

Below, we report the first-order coupling matrices, along with their corresponding eigenvalues and eigenvectors, for the fundamentals perturbed by Fermi type 2 resonances. The eigenvalues give first-order approximations to the band origins of the Fermi dyad, while the eigenvectors form a basis that allows first-order approximation of the contributions of the resonant fundamental and combination band to each peak. The latter not only qualitatively characterizes each observed peak, but may be used to estimate the intensity borrowing in each band due to the Fermi interaction.

- Fermi type 2 resonance due to $\omega_{19} + \omega_{20} \approx \omega_{10}$.

  First-order coupling matrix (all values in cm^{-1}):

  $$\begin{pmatrix} \tilde{\nu}_{19} + \tilde{\nu}_{20} + \tilde{X}_{19,20} & \frac{\phi_{10,19,20}}{\sqrt{8}} \\ \frac{\phi_{10,19,20}}{\sqrt{8}} & \tilde{\nu}_{10} \end{pmatrix} = \begin{pmatrix} 1033.26 & 8.21 \\ 8.21 & 1016.30 \end{pmatrix}$$

  Eigenvalues of first-order coupling matrix:

  $$\lambda_- = 1012.98\ \mathrm{cm}^{-1} \qquad \lambda_+ = 1036.58\ \mathrm{cm}^{-1}$$

  Eigenvectors of first-order coupling matrix:

  $$v_- = \begin{pmatrix} -0.9269 \\ -0.3752 \end{pmatrix} \qquad v_+ = \begin{pmatrix} 0.3752 \\ -0.9269 \end{pmatrix}$$

- Fermi type 2 resonance due to $\omega_{10} + \omega_{20} \approx \omega_{17}$.

  First-order coupling matrix (all values in cm^{-1}):

  $$\begin{pmatrix} \tilde{\nu}_{10} + \tilde{\nu}_{20} + \tilde{X}_{10,20} & \frac{\phi_{10,17,20}}{\sqrt{8}} \\ \frac{\phi_{10,17,20}}{\sqrt{8}} & \tilde{\nu}_{17} \end{pmatrix} = \begin{pmatrix} 1242.14 & -7.93 \\ -7.93 & 1245.10 \end{pmatrix}$$

  Eigenvalues of first-order coupling matrix:

  $$\lambda_- = 1235.55\ \mathrm{cm}^{-1} \qquad \lambda_+ = 1251.69\ \mathrm{cm}^{-1}$$

  Eigenvectors of first-order coupling matrix:

  $$v_- = \begin{pmatrix} -0.6390 \\ 0.7692 \end{pmatrix} \qquad v_+ = \begin{pmatrix} -0.7692 \\ -0.6390 \end{pmatrix}$$