# Supporting Information

# Ethyl + O<sub>2</sub> Reaction in Helium Nanodroplets: Infrared Spectroscopy of the Ethylperoxy Radical

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# **Optimized Geometries of Ethylperoxy Radical**

Units: Angstroms

# UHF-CCSD(T)-F12/cc-pVDZ-F12 Convergence: $10^{-8} E_h/a_0$

### Gauche

0	-1.349344997852	-0.544835159289	0.159158958398
0	-0.684186976215	0.476381885755	-0.343915580316
С	0.607919448080	0.607614779571	0.307837984722
С	1.539362694688	-0.504516361505	-0.120806863736
Η	0.426471401077	0.606324523727	1.382250710308
Η	0.958858163009	1.589346295787	-0.009851385922
Η	1.124830082693	-1.470018498337	0.165978936574
Η	1.689085348506	-0.487028752085	-1.200387698380
Η	2.507062451717	-0.379795581125	0.367283640165
Tra	ans		
0	-1.712967170671	0.098046241159	0.000000000000
0	-0.520698882244	-0.462817183701	0.0000000000000
С	0.519603099039	0.551695894696	0.0000000000000
С	1.845333932578	-0.173213466914	0.0000000000000
Η	0.373219394908	1.163681239127	0.889970212700
Η	0.373219394908	1.163681239127	-0.889970212700
Η	1.943984779911	-0.800011265727	0.886013665536
Η	1.943984779911	-0.800011265727	-0.886013665536
Н	2.656592691396	0.555314181179	0.000000000000

# UHF-CCSD(T)/ANO0 Convergence: $10^{-10} E_h/a_0$

Gauche

Ο	-1.356338826629	-0.558457943839	0.157369032229
0	-0.687342883492	0.495585246570	-0.344680691241
С	0.610058678860	0.605870219767	0.315578382053
С	1.546346357970	-0.508429494967	-0.126025466887
Η	0.434065618485	0.594668389381	1.397519267852
Η	0.975805741756	1.594715550410	0.012171881076
Η	1.129252792679	-1.484357762423	0.149107432349
Η	1.700394945839	-0.478945940031	-1.212027592277
Η	2.519247355846	-0.388454963543	0.369026951111

# Trans

-1.729137790213	0.106785735720	0.000000000000	
-0.518308175852	-0.477763980311	0.000000000000	
0.518703735845	0.549909106548	0.00000000000	
1.859332253054	-0.166218590366	0.000000000000	
0.376546745031	1.168030589271	0.894472399817	
0.376546745031	1.168030589271	-0.894472399817	
1.966461488311	-0.796558352427	0.891507499067	
1.966461488311	-0.796558352427	-0.891507499067	
2.667714817105	0.576212226842	0.000000000000	
	-1.729137790213 -0.518308175852 0.518703735845 1.859332253054 0.376546745031 0.376546745031 1.966461488311 1.966461488311 2.667714817105	-1.7291377902130.106785735720-0.518308175852-0.4777639803110.5187037358450.5499091065481.859332253054-0.1662185903660.3765467450311.1680305892710.3765467450311.1680305892711.966461488311-0.7965583524271.966461488311-0.7965583524272.6677148171050.576212226842	-1.7291377902130.1067857357200.00000000000-0.518308175852-0.4777639803110.000000000000.5187037358450.5499091065480.0000000000001.859332253054-0.1662185903660.0000000000000.3765467450311.1680305892710.8944723998170.3765467450311.168030589271-0.8944723998171.966461488311-0.7965583524270.8915074990671.966461488311-0.796558352427-0.8915074990672.6677148171050.5762122268420.00000000000

# **UHF-CCSD(T)/ANO1** Convergence: 10<sup>-9</sup> E<sub>h</sub>/a<sub>0</sub>

# Gauche

0	-1.350000256872	-0.548031220536	0.158876070824
0	-0.684096608616	0.480905668596	-0.344214824758
С	0.608157805389	0.607726790519	0.309588709440
С	1.539481674900	-0.505808252507	-0.121855798879
Η	0.428028505132	0.604912408946	1.384598114125
Η	0.962689861385	1.589880590180	-0.004735591326
Η	1.123326377914	-1.472009834660	0.163098259675
Η	1.688102983861	-0.486860415510	-1.202296033251
Η	2.508870285245	-0.384118139025	0.365492184673
Tra	ans		
0	-1.716551044757	0.099351853726	0.0000000000000
0	-0.519107392251	-0.465666284593	0.000000000000
С	0.519017564413	0.551975850628	0.000000000000
С	1.847674049625	-0.171887142349	0.0000000000000
Η	0.374062712939	1.164733571588	0.890083255544
Η	0.374062712939	1.164733571588	-0.890083255544
Η	1.947096305093	-0.799382169230	0.886352804652
Η	1.947096305093	-0.799382169230	-0.886352804652
Η	2.659412147779	0.557321837327	0.000000000000

### UHF-CCSD(T)/haug-cc-pVTZ

Convergence:  $10^{-9} E_h/a_0$ 

Gauche

0	-1.354794613332	-0.545350440343	0.160241162915
0	-0.683785716982	0.478469082536	-0.347194357259
С	0.610539843857	0.607480162171	0.311691829165
С	1.542613562822	-0.505912907891	-0.122045900514
Η	0.424139973120	0.601444546389	1.386255322641
Η	0.961555749872	1.591645200510	-0.002496155542
Η	1.126552866853	-1.473646775686	0.160345775965
Η	1.692897488490	-0.483349192169	-1.202842302925
Η	2.511374378446	-0.383982018761	0.367738653223
Tra	ans		
0	-1.718706182605	0.098785803407	0.0000000000000
0	-0.520527169518	-0.465308402019	0.000000000000
С	0.521835168675	0.554355650677	0.000000000000
С	1.849373528819	-0.173593426763	0.0000000000000
Η	0.373942277489	1.165468529994	0.891489496457
Η	0.373942277489	1.165468529994	-0.891489496457
Η	1.947167548226	-0.801326123021	0.887171521232
Η	1.947167548226	-0.801326123021	-0.887171521232
Η	2.662462875786	0.555024229089	0.000000000000

#### **Comparisons of Harmonic Frequencies**

Sensitivity of the VPT2+K predictions to the harmonic frequencies was explored (Fig. S1). The four simulations for each conformer are completely analogous to each other, aside from using a different set of harmonic frequencies and intensities. We also note that these simulations are performed with semi-diagonal quartic force fields, where the cubic and quartic force constants are in the CCSD(T)/ANO0 normal coordinates. The number of bands from each conformer is nearly unchanged for the three levels of theory, and the relative intensities are also similar. However the differences in the zeroth-order frequencies influence the ordering of the bands. Between the hybrid simulations, which use at least triple-zeta quality harmonic

frequencies, the position of any given transition changes by less than 10 cm<sup>-1</sup>. It can be seen that CCSD(T)/ANO0 harmonic frequencies lead to a (sometimes) severe overestimation of the transition frequencies.



**Figure S1:** Infrared depletion spectrum of ethylperoxy, measured on mass channel 45 u, using DTAP, and VPT2+K simulations. The basis sets used for the harmonic frequencies and intensities are indicated for each pair of simulations (with the exception that the cc-pVDZ-F12 simulations used the haug-cc-pVTZ intensities). The *trans* simulations are in blue, while the *gauche* simulations are in pink.

#### **Numerical Accuracy of Force Constants**

The numerical accuracy of our normal coordinate force constants, which were determined by numerical differentiation of analytic internal coordinate gradients, followed by numerical transformation into normal coordinates, was benchmarked against CFOUR's standard semidiagonal quartic force field recipe, based upon analytic second derivatives. We computed quartic normal coordinate force fields for several small molecules: water, formaldehyde, hydrogen peroxide, and formic acid. The differences between our force constants and CFOUR's force constants were about  $\pm 0.01$  cm<sup>-1</sup> for quadratic and  $\pm 0.2$  cm<sup>-1</sup> for cubic and quartic. We also checked the correctness of the ethylperoxy anharmonic internal force constants by simply transforming them into the CCSD(T)/ANO0 normal coordinates. The agreement with CFOUR's force constants was excellent.

#### Four Variations of Force Field Transformation

The accuracy of different variations of the transformation from internal coordinates to normal coordinates was investigated (Tables S1-4). In these tables, the column "ANOO" contains the CCSD(T)/ANO0 force constants in their original normal coordinates, ordered by best match to the CCSD(T)-F12 normal coordinates. Four different variations of the transformation into the CCSD(T)-F12 normal coordinates are defined by the reference structure used to compute the L-tensor elements and by the set of quadratic internal force constants used in the transformation equations. These four variations are named as follows: ANO0 reference structure and ANO0 quadratic force constants (var-1), F12 reference structure and F12 quadratic force constants (var-2), F12 reference structure and ANO0 quadratic force constants (var-3), ANO0 reference

structure and F12 internal quadratic force constants (var-4). The column labeled "F12" contains anharmonic normal coordinate force constants evaluated via finite differences of CCSD(T)-F12/cc-pVDZ-F12 energies. Cubic and quartic force constants calculated in this manner are typically accurate to 1 cm<sup>-1</sup> (sometimes more numerical error for very low frequency coordinates, such as the torsions 20 and 21).

The force constants transformed with the var-2 procedure are usually very similar to those transformed with var-3; likewise, var-1 force constants are similar to var-4. This indicates that the contribution to these higher order force constants from the quadratic internal coordinate force constants is small. Procedures var-2 and var-3 are quite a bit better overall than var-1 and var-4. It is apparent that their use of the ANO0 equilibrium geometry for determination of the L-tensor elements is largely responsible for their deficiencies. For many normal coordinates, it can be seen that the transformed force constants are not greatly different. This is generally because the two sets of normal coordinates are very similar. Sometimes the transformed force constants are superior, and sometimes the force constants, the advantages of coordinate transformation are striking, such as for the antisymmetric CH stretching (i=14,15) cubic force constants of the *gauche* conformer (Table S3). In this instance, the transformation puts the force constants into excellent agreement with the true CCSD(T)-F12 values.

i	Γ	ANO0	var-1	var-2	var-3	var-4	F12
1	<i>a'</i>	-787.3	-796.3	-794.0	-794.1	-796.3	-783.1
2	<i>a'</i>	1335.8	1351.2	1351.0	1351.0	1351.2	1332.4
3	<i>a'</i>	1051.6	1067.2	1067.3	1067.3	1067.2	1054.9
4	<i>a'</i>	35.1	18.3	17.4	16.8	18.8	17.3
5	<i>a'</i>	-62.1	-63.2	-62.3	-63.3	-62.3	-62.4
6	<i>a'</i>	-101.4	-109.4	-107.1	-109.9	-106.6	-106.2
7	<i>a'</i>	-12.4	-14.9	-16.0	-19.6	-11.4	-21.4
8	<i>a'</i>	334.1	346.9	345.8	346.5	346.2	410.9
9	<i>a'</i>	95.6	-86.0	-89.3	-90.2	-85.2	-86.9
10	<i>a'</i>	-93.2	-90.2	-87.3	-87.3	-90.2	-83.3
11	<i>a'</i>	131.6	144.0	132.8	134.5	142.2	134.0
12	<i>a</i> ′	59.0	57.8	60.0	61.2	56.8	58.2
13	<i>a</i> ′	-10.7	-1.2	-9.8	-11.1	0.4	-11.6
RM	SD	53.1	9.1	7.5	7.5	9.3	_

TABLE. S1: Comparisons of *trans*  $\phi_{iii}$  (cm<sup>-1</sup>) for four methods of transforming from internal to normal coordinate force constants RMSD excludes the O-O stretch (*i* = 8).

i	Г	ANO0	var-1	var-2	var-3	var-4	F12
1	<i>a'</i>	553.3	558.4	557.8	557.8	558.4	548.8
2	<i>a'</i>	512.2	521.3	521.1	521.2	521.3	510.6
3	<i>a'</i>	322.6	328.5	328.5	328.5	328.5	322.9
4	<i>a'</i>	15.3	12.5	11.6	12.1	12.0	1.5
5	<i>a'</i>	13.6	14.3	13.6	14.1	13.9	2.4
6	<i>a'</i>	32.3	34.0	32.7	32.9	33.8	31.9
7	<i>a'</i>	66.5	71.6	70.9	71.4	71.0	69.7
8	<i>a'</i>	106.0	106.8	106.3	106.3	106.8	120.1
9	<i>a'</i>	12.6	14.7	14.6	14.7	14.7	13.8
10	<i>a'</i>	37.8	42.1	41.4	41.4	42.1	39.6
11	<i>a'</i>	97.7	99.1	99.6	100.1	98.5	99.2
12	<i>a'</i>	6.3	5.9	6.7	6.4	6.1	6.0
13	<i>a'</i>	69.4	68.0	71.3	69.3	69.9	70.8
14	<i>a</i> "	302.8	314.7	314.8	314.9	314.7	309.7
15	<i>a</i> "	310.9	323.7	324.1	324.0	323.8	318.1
16	<i>a</i> "	6.3	5.7	4.6	4.4	5.8	-9.7
17	<i>a</i> "	57.2	58.3	57.3	58.9	57.5	56.6
18	<i>a</i> "	67.9	64.3	63.4	64.2	63.5	61.5
19	<i>a</i> "	293.9	295.8	297.1	299.2	293.7	296.7
20	<i>a</i> "	3234.8	3474.0	3509.2	3520.2	3463.2	3502.2
21	<i>a</i> "	541.3	628.5	744.0	652.2	716.7	746.7
RM	ISD	77.2	27.9	6.3	22.4	12.7	_

TABLE. S2: Comparisons of *trans*  $\phi_{iiii}$  (cm<sup>-1</sup>) for four methods of transforming from internal to normal coordinate force constants RMSD excludes the O-O stretch (*i* = 8).

i	Γ	ANO0	var-1	var-2	var-3	var-4	F12
1	<i>a'</i>	258.3	165.1	165.7	165.7	165.1	162.8
2	<i>a'</i>	-1329.9	-1338.4	-1337.8	-1337.8	-1338.4	-1321.7
3	<i>a'</i>	-1063.7	-1078.7	-1078.7	-1078.7	-1078.7	-1065.9
4	<i>a'</i>	-55.0	-54.5	-53.5	-54.5	-53.6	-53.2
5	<i>a'</i>	19.4	29.8	29.2	29.5	29.5	30.8
6	<i>a'</i>	-100.2	-108.3	-107.7	-110.3	-105.8	-107.4
7	<i>a'</i>	-2.6	2.1	-9.4	-10.5	3.1	-10.5
8	<i>a'</i>	241.7	197.8	199.2	199.4	197.6	242.6
9	<i>a'</i>	-100.3	130.3	128.0	129.9	128.4	125.7
10	<i>a'</i>	-11.7	-28.8	-30.4	-30.6	-28.6	-25.2
11	<i>a'</i>	139.1	146.7	145.8	147.6	145.0	145.8
12	<i>a'</i>	40.2	43.3	42.8	43.0	43.1	39.8
13	<i>a'</i>	54.5	53.8	56.2	56.2	53.7	57.0
14	<i>a</i> "	344.9	260.5	261.4	261.4	260.5	257.2
15	<i>a</i> "	227.7	210.0	209.4	209.4	210.0	206.0
16	<i>a</i> "	11.3	-8.9	-10.5	-10.7	-8.7	-9.8
17	<i>a</i> "	-9.0	13.5	13.3	14.7	12.2	17.4
18	<i>a</i> "	-12.4	42.9	38.7	39.5	41.9	47.0
19	<i>a</i> "	22.0	18.0	18.4	19.6	16.8	16.0
20	<i>a</i> "	9.3	158.3	7.9	7.4	158.2	7.0
21	<i>a</i> "	41.9	43.2	46.8	47.2	46.5	43.7
RM	ISD	60.7	34.4	5.5	5.6	34.4	-

TABLE. S3: Comparisons of *gauche*  $\phi_{iii}$  (cm<sup>-1</sup>) for four methods of transforming from internal to normal coordinate force constants. RMSD excludes the O-O stretch (*i* = 8).

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i	Γ	ANO0	var-1	var-2	var-3	var-4	F12
1	<i>a'</i>	309.2	323.4	323.3	323.3	323.4	318.3
2	<i>a'</i>	509.7	515.1	514.8	514.8	515.1	506.0
3	<i>a'</i>	332.3	338.1	338.2	338.1	338.1	332.6
4	<i>a'</i>	8.9	8.5	7.5	7.8	8.2	-3.9
5	<i>a'</i>	5.7	8.3	7.6	7.9	7.9	-1.1
6	<i>a'</i>	34.1	35.6	34.8	35.0	35.3	34.3
7	<i>a'</i>	70.1	73.8	72.7	73.4	73.1	71.0
8	<i>a'</i>	69.5	60.6	60.7	60.8	60.5	69.0
9	<i>a'</i>	23.7	28.3	28.2	28.3	28.2	27.2
10	<i>a'</i>	21.1	24.4	24.1	24.1	24.4	22.3
11	<i>a'</i>	59.0	60.5	60.7	60.8	60.4	60.5
12	<i>a'</i>	41.4	41.4	43.2	42.4	42.1	42.4
13	<i>a'</i>	49.6	44.8	45.9	45.5	45.1	45.9
14	<i>a</i> "	332.1	313.5	314.2	314.1	313.5	309.5
15	<i>a</i> "	314.0	333.2	333.2	333.2	333.2	328.1
16	<i>a</i> "	8.2	5.6	4.9	5.1	5.5	-3.8
17	<i>a</i> "	62.7	64.6	63.4	64.4	63.6	61.1
18	<i>a</i> "	28.1	20.9	20.6	21.0	20.6	21.3
19	<i>a</i> "	230.2	238.2	239.2	241.2	236.2	239.0
20	<i>a</i> "	3370.0	3574.3	3611.3	3626.0	3559.8	3607.3
21	<i>a</i> "	407.6	401.2	441.8	414.4	427.5	439.3
RM	ISD	54.2	12.4	5.0	8.6	12.1	-

TABLE. S4: Comparisons of *gauche*  $\phi_{iiii}$  (cm<sup>-1</sup>) for four methods of transforming from internal to normal coordinate force constants RMSD excludes the O-O stretch (*i* = 8).

#### **Details Regarding Full Quartic Force Field Calculations**

To compute full quartic force fields of *trans-* and *gauche-*ethylperoxy, displacements were made in all 3N-6 internal (z-matrix) coordinates. Step sizes used were 0.005 Å for bond lengths and 0.25 degrees for bond angles and dihedral angles. Up to two positive and negative steps were taken in single internal coordinates, and single positive and negative steps were taken simultaneously in two and three internal coordinates. No advantage was taken of symmetry to reduce the number of displacements needed; although, abelian computational symmetry could be used for all of the C<sub>s</sub> symmetry displacements of the *trans* conformer. A total of 11564 displaced gradients were computed for each conformer. CFOUR was directed to compute analytic energy gradients and to transform them into z-matrix coordinates by providing z-matrix coordinate input, requesting geometry optimization, and including the keyword GEO\_MAXSTEP=1. Gradients were read from the GRDINT files written by CFOUR.<sup>1</sup>

An analytic gradient vector of length 3N-6 is determined at each displacement. For each component of this vector, 1D, 2D, and 3D, in internal coordinates, were constructed from its values at equilibrium (effectively zero) and at displacements along all 3N-6 internal coordinates. These grids were constructed for every possible combination of 1, 2, and 3 different internal coordinates. In Mathematica, low-order polynomial interpolation was applied to each rectangular grid with the "Interpolation" function. A necessary condition to use Mathematica's interpolation function on multidimensional data is that the grids be rectangular. This implies that the grids in 2 and 3 normal modes may only include the gradients from points displaced by  $\pm 1$  units. For each interpolated grid, a Taylor series expansion was constructed about the equilibrium using the "Series" function.<sup>2</sup> Then quadratic, cubic, and quartic force constants are extracted from each Taylor series. Once this has been performed on all possible grids, some types of force constants

will have been determined redundantly; these are averaged together. Comparing the values of these force constants also provides a numerical consistency check on the force field. This kind of diagnostic is also reported by CFOUR for quartic force constants of the iijj type. We found that this interpolation scheme allows for accurate determination of force constants. It is not as sensitive to step size or the number of grid points as direct least squares fitting of Taylor polynomials, and it is more straightforward to apply than central difference formulas.

The internal coordinate force constants are converted into atomic units. The L-tensor elements are then evaluated via central finite differences. Up to third derivatives of the internal coordinates with respect to the normal coordinates are necessary to transform a full quartic force field.<sup>3</sup> In order to evaluate these, the dimensionless normal coordinates, in the form of Cartesian displacement vectors, are read from the QUADRATURE file that CFOUR writes after a harmonic frequency calculation. Small steps in the normal coordinates are made by adding the normal coordinate vectors to the cartesian coordinates of the equilibrium geometry. About 0.001 units is found to be satisfactory. The values of the internal coordinates are measured at these displaced geometries. Once all elements of the L-tensor are determined, the force constants in normal coordinates are straightforwardly determined using algebraic equations.<sup>3</sup>

#### **Mass Spectrometry**

A series of mass spectra for the *n*-propylnitrite (PRONO) experiments are presented below (Fig. S2). Trace (a) shows the neat droplet beam. When droplets are doped with the PRONO precursor (trace b), some parent ion signal appears at 90 u and also deprotonated signals at 89 and 88 u. These signals diminish when the precursor is decomposed in the heated pyrolysis source (trace c). Also note the increase in 27 u and 30 u upon heating the source. The only

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obvious change upon adding O<sub>2</sub> (trace d) is the growth of 32 u; the enhancement of 45 u, the chosen mass channel for ethylperoxy spectroscopy, is slight. The pyrolysis current was chosen to maximize the ethylperoxy depletion signal; the optimal value for PRONO was found to be 30 A, somewhat higher than for the di-*tert*-amyl peroxide (DTAP) precursor, which optimized at 20 A.



**Figure S2:** HENDI mass spectra of (a) neat droplet beam (b) cold PRONO (c) PRONO with 30 A pyrolysis current (d) PRONO with 30 A pyrolysis current with O<sub>2</sub>.

### **Infrared Spectroscopy**

An infrared spectrum of *n*-propylnitrite was collected (Fig. S3). Several skeletal and nitrite torsional isomers are expected to be populated in the PRONO sample. This spectrum could be modeled as the sum of several conformer specific spectra, with appropriate Boltzmann-weights. We make no attempt to assign these features.



**Figure S3:** Infrared spectrum of the *n*-propylnitrite precursor, measured on mass channel 29 u, in the region hosting ethylperoxy radical features. It is likely that several rotamers are contributing to this spectrum.

#### References

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