

Does acetone react with HO₂ in the upper-troposphere?

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Uncertainties in the theoretical predictions

As detailed in the main paper, no experimental evidence currently exists that shows HO₂ radicals constitute an important chemical sink for acetone in the atmosphere. The inclusion of this process in atmospheric chemical models, then, relies on the quantum chemical characterization of the reaction process.

Summary of reaction scheme and current theoretical data

The formation of a hydrogen-bonded complex between acetone and HO₂ has been described by several authors (Aloisio et al.,¹ Hermans et al.,² Cours et al.³) and has been measured by others (Grieman et al.,⁴ this work). The stability of the acetone--HO₂ complex ($\Delta H_r(0K)$ see table 1) was predicted to lie between 34 and 44 kJ mol⁻¹, with the most reliable levels of theory agreeing on a value of 40 to 42 kJ mol⁻¹, while an spectroscopic van't Hoff analysis by Grieman et al.⁴ suggests a $\Delta H_r(245K)$ of -35.4 ± 2.0 kJ mol⁻¹. The complex formation is a barrierless reaction owing to the long-range attractive forces involved, and proceeds very rapidly to establish an equilibrium between the separated reactants and the complex. As an atmospheric sink for acetone, however, the complex formation is not effective as it does not chemically transform the acetone molecule.

The addition of HO₂ across the carbonyl double bond leads to the formation of α -OH alkylperoxy radicals (CH₃)₂C(OH)OO•; this reaction will typically proceed starting from the pre-reactive H-bonded complex discussed above. The α -OH alkylperoxy radicals formed can decompose thermally, regenerating the acetone + HO₂ molecules. The energy barrier for decomposition of the intermediate peroxy radicals are predicted to lie between 36 and 50 kJ mol⁻¹ (see table 2), with the most reliable levels of theory agreeing on a barrier of 46-48 kJ mol⁻¹.

Subsequent reaction of the peroxy radical with coreactants such as NO, HO₂ and/or RO₂ will compete with the thermal decomposition of the α -OH alkylperoxy radicals, the former reactions chemically removing the acetone and providing a sink, while the latter reaction regenerates the acetone+HO₂. The efficiency of chemical removal depends on the ratio of the pseudo-first order rates of bimolecular removal of the α -OH alkylperoxy radical versus its thermal decomposition. For the energy barriers predicted for decomposition, thermal decomposition at room temperature is fast, and expected to easily outrun bimolecular reactions. At these temperatures, then, removal by acetone through reaction with HO₂ and subsequent chemical transformation of the α -OH alkylperoxy radicals is not expected to contribute in the atmosphere. In contrast, at lower temperature, the rate of decomposition of the alkylperoxy radicals is slower, and the likelihood of undergoing a bimolecular reaction increases. For a given concentration of coreactants found in the atmosphere, the removal through bimolecular reactions then depends on the concentration of α -OH alkylperoxy radicals, or, given that the alkylperoxy radicals can decompose back to acetone+HO₂, on the equilibrium reaction between acetone + HO₂ with the α -OH alkylperoxy radicals. A high-pressure thermal equilibrium established between these two sides represents the most favorable situation for competing bimolecular reactions; all effects disturbing this equilibrium (e.g. pressure effects, removal of the adduct radicals at faster rates than their formation, etc.)

lead to lower/depleted concentrations of peroxy radicals, thus lowering the impact of bimolecular reactions, and hence result in a lower contribution of the HO₂ channel as an acetone sink compared to the traditional acetone sinks operating in the atmosphere.

The key parameter in describing the efficiency of the HO₂ pathway as a sink for acetone in the atmosphere is then the equilibrium constant $K_{eq} = [\text{acetone}][\text{HO}_2]/[(\text{CH}_3)_2\text{C}(\text{OH})\text{OO}^\bullet]$ describing the fraction of acetone present as the hydroxy-alkylperoxy radical adducts. The separated reactants are favored entropically, but the adduct is favored energetically. The equilibrium will shift towards the adduct at lower temperatures, increasing the importance of this sink; Hermans et al.² proposed that at temperatures below 220K, the HO₂ route would provide a non-negligible sink for acetone. At such low temperatures the equilibrium constant depends critically on the energy difference between adduct and free reactants. Indeed, at 220K, a 1 kJ mol⁻¹ uncertainty on the energy difference constitutes an uncertainty of a factor of 1.73 on the equilibrium constant. The values of reported by Hermans et al.² (see table 3), seem well-converged at 58 to 59 kJ mol⁻¹; however, these calculations all rely on B3LYP geometries and employ similar extrapolation schemes to estimate a CCSD(T) energy with a large basis set. The energies reported by Cours et al.³ based on MP2 geometries and employing a CCSD(T)/6-311G(d,p) methodology as their best method show a well depth of only 47 kJ mol⁻¹. The 11 kJ mol⁻¹ difference in estimated well depth between Hermans et al. and Course et al. implies an uncertainty of a factor of ~400 on the equilibrium constant at 220K, with the Course et al. values rendering the HO₂ channel negligible as an acetone sink across all regions of the atmosphere.

The quantum chemical methodologies used in the aforementioned studies employ a lower level of theory to obtain molecular geometries (usually DFT or MP2), followed by single-point energy calculations at a higher level of theory. Multiple single-point energy calculations are often combined to estimate the energy that would be obtained at a higher, computationally unattainable methodology; e.g. the G2M method used by Hermans et al.² employs CCSD(T) calculations with a small basis set combined with MP2 calculations at a small and large basis set, to estimate the CCSD(T) energy for the large basis set. Such extrapolation schemes carry additional uncertainties, but are shown to yield reliable results for a wide variety of chemical reactions, even if they fail for some reactions.

Quantum chemical calculations

To gain further insight in the uncertainties on the theoretical predictions, we performed additional quantum chemical calculations to probe specific aspects of the predictions. To study the impact of the geometry used, we compared the geometries obtained at three levels of theory: B3LYP/cc-pVTZ (as used by Hermans et al.²), MP2/6-311G(d,p) (as used by Cours et al.³), and M05-2X/aug-cc-pVTZ (this work).

To avoid incurring additional uncertainties due to extensive energy extrapolation schemes, we calculate single point CCSD(T) energies directly with large basis sets, up to aug-cc-pVTZ; such calculations were computationally infeasible at the time of the Hermans et al.² publication. Finally, the CCSD(T) energies are then extrapolated to infinite basis set using the aug-Schwartz4 scheme proposed by Martin et al.;⁵ note that extrapolating to the aug-cc-pV ∞ Z basis set using only aug-cc-pVDZ and -pVTZ data is not optimal, but is done here to illustrate the dependence on the basis set size. A more accurate estimation could be done if aug-cc-pVQZ data was available, but such calculations are outside our computing budget.

Geometry and frequency calculations using M05-2X, B3LYP and MP2 were performed using Gaussian-09;⁶ the coupled-cluster calculations were ROHF-UCCSD(T)⁷ single point energy calculations performed using Molpro-2010.⁸ M05-2X/aug-cc-pVTZ zero-point vibrational energies were scaled by 0.964 as listed by Zheng et al.;⁹ MP2/6-311G(d,p) ZPE are scaled by 0.9748 as derived by Scott and Radom;¹⁰ B3LYP/cc-pVTZ ZPE are scaled here by 0.985 as

estimated from Zheng et al.⁹ In this work, we did not explicitly account for degrees of freedom for internal rotation in acetone as described by Hermans et al.² Briefly, Hermans et al. found that an improved description of these internal modes changed the relative energy of reactants versus adduct by ~ 0.4 kJ mol⁻¹. For our current analysis, all levels of theory are expected to yield near-identical correction terms, canceling out in the assessment of the properties relative to the methodology used.

Discussion

A first conclusion to be drawn is that the large difference between the predictions of Cours et al.³ and Hermans et al.² is due entirely to an insufficient basis set size (6-311G(d,p)) in the calculations by Cours et al.; single-point energy calculations using more appropriate basis sets such as aug-cc-pVDZ and higher (see tables below) yield more comparable relative energies across the B3LYP geometries (Hermans et al.) and the MP2 geometries (Cours et al.). This observation also indicates that the relative energies can be fairly sensitive to basis set size. In view of the above, we disregard the Cours et al. energy predictions, though we will continue examining the MP2-based geometries.

A second observation is that the uncertainties in the quantum chemical calculations are mostly due to the change in chemical bonding between HOO[•] and acetone on the one hand, and (CH₃)₂C(OH)OO[•] and its decomposition TS on the other hand. The reaction enthalpy for the formation of the pre-reactive complex acetone--HO₂ are fairly similar across all methodologies (Table 1), as are the barrier height for decomposition of the adduct (Table 2, though logically we already see more impact by the change in bonding). The largest differences in predicted relative energies are found between the separated reactants and the adducts (Table 3), where a double bond is reduced to a single bond, a new carbon-oxygen bond is formed, and the substituent neighborhood is changed significantly.

Thirdly, we observe that all three sets of geometries, i.e. MP2, B3LYP and M05-2X show similar relative energies, with similar trends as to the well-depths and barrier heights with respect to basis set size in the single-point calculations. On an absolute scale, the B3LYP geometries seem to be the best, where we use the metric that these geometries yield the lowest absolute ROHF-UCCSD(T) energies, and are hence closest to the true energy minimum on the ROHF-UCCSD(T) potential energy surface for the structures examined. The absolute energy difference between the different geometry sets becomes smaller as the size of the basis set used in the CCSD(T) calculations increases.

The relative energy of the adduct with respect to the separated reactants reduces quite significantly upon increasing the basis set from double to triple zeta quality, on average by 4.3 kJ mol⁻¹, with the largest change of nearly 5 kJ mol⁻¹ for the B3LYP geometries; this implies a reduction in the equilibrium constant at 220K of 1 order of magnitude; note that these uncertainties don't necessarily translate to other compounds such as HCHO or CH₃CHO. Uncertainties of this order were already indicated by Hermans et al. Our current best level of theory available, i.e. B3LYP geometries and ROHF-CCSD(T) single-point energies extrapolated to infinite basis set, suggests a well depth of 54.4 kJ mol⁻¹, 4.2 kJ mol⁻¹ below the best G2Mc values of Hermans et al. The current best level of theory without extrapolated energies (ROHF-CCSD(T)/aug-cc-pVTZ//B3LYP) has a well depth of 56.4 kJ mol⁻¹, 2.2 kJ mol⁻¹ below the Hermans et al. values. At 220K, uncertainties of 4.2 and 2.2 kJ mol⁻¹ on the adduct stability implies an uncertainty of a factor 9.9 and 3.3, respectively, on the equilibrium constant; at 200K the uncertainties are a factor of 12.5 and 3.8, respectively.

Conclusions

The uncertainties found for the addition well depth in the current set of calculations, combined with the high sensitivity of the equilibrium constant on this well depth at the low temperatures in the atmosphere where this reaction is thought to be important, indicates that the role of this reaction as an acetone sink is not fully elucidated yet. The best available calculations suggest that the HO₂-channel is at best a minor sink throughout the atmosphere. Obviously these calculations carry their own uncertainty, but the trend seems to be that increasing the level of theory decreases the addition well depth and hence the equilibrium constant. No experimental evidence was found for the HO₂ addition to acetone, in this or earlier work; however, as discussed in the main article, this could be also be due to other interferences, or lack of sensitivity to the reaction examined. Further theoretical and experimental work is needed to determine the impact of this acetone sink more accurately. It should be noted that the uncertainties evident in our current set of calculations do not impact the importance of the HO₂ addition on carbonyl compounds as relevant in higher-temperature hydrocarbon autoxidation processes, nor are they of such extend that they invalidate the agreement between theory and experiment at 300K for HCHO and CH₃CHO + HO₂ (see Hermans et al.²). At the low temperatures of the tropopause, however, small changes in energy have a much more pronounced impact on the predicted equilibrium constants.

Table 1: Stability of the acetone--HO₂ H-bonded complex (kJ/mol; ZPE-corrected) at various levels of theory.

Methodology	Relative energy	Reference
M05-2X/aug-cc-pVTZ	42.3	This work
B3LYP/6-311++G(3df,3pd)	37.2	Aloisio et al.
B3LYP/cc-pVTZ	39.8	Hermans et al. (recalculated)
MP2/6-311G(d,p)	41.4	Cours et al. (recalculated)
PMP2/6-311G(d,p)//MP2	36.0	Cours et al.
PMP4/6-311G(d,p)//MP2	35.1	Cours et al.
CBS-QB3	39.7	Hermans et al.
G3	41.4	Hermans et al.
G2Mc//B3LYP (estimated)	41.0	Hermans et al.
CCSD(T)/6-311G(d,p)//MP2	34.1	Cours et al.
CCSD(T)/aug-cc-pVDZ//M05-2X	43.7	This work
CCSD(T)/aug-cc-pVDZ//B3LYP	42.6	This work
CCSD(T)/aug-cc-pVDZ//MP2	40.8	This work
CCSD(T)/aug-cc-pVTZ//M05-2X	42.3	This work
CCSD(T)/aug-cc-pVTZ//B3LYP	41.1	This work
CCSD(T)/aug-cc-pVTZ//MP2	39.8	This work
CCSD(T)/aug-Schwartz4(DT)//M05-2X	41.9	This work
CCSD(T)/aug-Schwartz4(DT)//B3LYP	40.7	This work
CCSD(T)/aug-Schwartz4(DT)//MP2	39.4	This work

Table 2: Energy barrier for decomposition of the α -OH-alkylperoxy radical of acetone (kJ/mol; ZPE-corrected) forming the H-bonded complex.

Methodology	Relative energy	Reference
M05-2X/aug-cc-pVTZ	45.9	This work
B3LYP/cc-pVTZ	26.1	Hermans et al. (recalculated)
MP2/6-311G(d,p)	39.0	Cours et al. (recalculated)
PMP2/6-311G(d,p)//MP2	35.9	Cours et al.
PMP4/6-311G(d,p)//MP2	37.1	Cours et al.
CBS-QB3	48.1	Hermans et al.
G3	47.7	Hermans et al.
G2Mc//B3LYP (estimated)	46.7	Hermans et al.
CCSD(T)/6-311G(d,p)//MP2	44.9	Cours et al.
CCSD(T)/aug-cc-pVDZ//M05-2X	49.7	This work
CCSD(T)/aug-cc-pVDZ//B3LYP	48.8	This work
CCSD(T)/aug-cc-pVDZ//MP2	50.0	This work
CCSD(T)/aug-cc-pVTZ//M05-2X	47.7	This work
CCSD(T)/aug-cc-pVTZ//B3LYP	46.9	This work
CCSD(T)/aug-cc-pVTZ//MP2	48.0	This work
CCSD(T)/aug-Schwartz4(DT)//M05-2X	47.0	This work
CCSD(T)/aug-Schwartz4(DT)//B3LYP	45.9	This work
CCSD(T)/aug-Schwartz4(DT)//MP2	47.3	This work

Table 3: ZPE-corrected potential energy difference (kJ/mol; ZPE-corrected) between the α -OH-alkylperoxy radical formed from acetone, and the limit of infinite separation of acetone + HO₂.

Methodology	Relative energy	Reference
M05-2X/aug-cc-pVTZ	66.4	This work
B3LYP/cc-pVTZ	31.0	Hermans et al. (recalculated)
MP2/6-311G(d,p)	48.3	Cours et al. (recalculated)
PMP2/6-311G(d,p)//MP2	48.2	Cours et al.
PMP4/6-311G(d,p)//MP2	43.5	Cours et al.
CBS-QB3	58.2 ^a	Hermans et al.
G3	58.2 ^a	Hermans et al.
G2Mc//B3LYP (estimated)	58.6 ^a	Hermans et al.
CCSD(T)/6-311G(d,p)//MP2	46.9	Cours et al.
CCSD(T)/aug-cc-pVDZ//M05-2X	62.2	This work
CCSD(T)/aug-cc-pVDZ//B3LYP	61.3	This work
CCSD(T)/aug-cc-pVDZ//MP2	58.5	This work
CCSD(T)/aug-cc-pVTZ//M05-2X	57.6	This work
CCSD(T)/aug-cc-pVTZ//B3LYP	56.4	This work
CCSD(T)/aug-cc-pVTZ//MP2	55.2	This work
CCSD(T)/aug-Schwartz4(DT)//M05-2X	55.4	This work
CCSD(T)/aug-Schwartz4(DT)//B3LYP	54.4	This work
CCSD(T)/aug-Schwartz4(DT)//MP2	54.0	This work

^a ~0.1 kcal/mol was subtracted to correct for the change in zero-point vibrational energy incurred by the rigorous treatment of internal rotors (see Hermans et al.²).

References

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Quantum chemical data

a) M05-2X/aug-cc-pVTZ geometries

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acetone.C2v
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E(RM052X/Aug-CC-pVTZ) (Hartree): -193.20110143
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -192.67623312
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -192.85141364
E(ROHF-UCCSD(T)/Aug-CC-pVQZ) (Hartree): -192.90077027
Point group : C2V
Electronic state : 1-A1
Cartesian coordinates (Angs):
  C      0.000000      0.000000      0.183704
  C      0.000000      1.279595     -0.609907
  C      0.000000     -1.279595     -0.609907
  H     -0.876208      1.311184     -1.255514
  H      0.000000      2.129554      0.061668
  H      0.876208      1.311184     -1.255514
  H     -0.876208     -1.311184     -1.255514
  H      0.876208     -1.311184     -1.255514
```

H	0.000000	-2.129554	0.061668	
O	0.000000	0.000000	1.389423	
Rotational constants (GHz):	10.2589600	8.6443800	4.9773600	
Vibrational harmonic frequencies (cm-1):				
147.9093	133.8503		375.9216	
490.4565	544.5136		817.0493	
896.1726	908.2528		1096.8960	
1137.8371	1269.2155		1402.1687	
1414.6413	1479.9781		1486.5762	
1490.6464	1509.5899		1841.8479	
3088.4451	3094.3905		3147.0705	
3154.2036	3199.7863		3200.8963	
Zero-point correction (Hartree): 0.084703				

acetone..HO2.a

E(UM052X/Aug-CC-pVTZ) (Hartree): -344.16372115
 E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.29510528
 E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.59606141
 Electronic state : 2-A
 Cartesian coordinates (Angs):

C	1.147961	-0.068815	-0.015630	
O	0.317517	-0.955483	-0.036684	
H	-1.386091	-0.822256	-0.083699	
O	-2.367742	-0.691078	-0.087467	
O	-2.545419	0.581694	0.150970	
C	0.770157	1.377816	-0.085325	
H	1.064768	1.758134	-1.063750	
H	-0.298844	1.498860	0.048684	
H	1.325048	1.945826	0.658285	
C	2.608322	-0.392041	0.079665	
H	3.170063	0.181150	-0.654543	
H	2.964309	-0.089840	1.064225	
H	2.767258	-1.454696	-0.056013	
Rotational constants (GHz):	7.4197500	1.5132100	1.2812900	
Vibrational harmonic frequencies (cm-1):				
48.9035	69.0109		91.5689	
101.5918	126.7144		145.1437	
221.9271	392.5105		492.6653	
562.2234	725.8026		829.2518	
899.3746	929.6109		1105.6714	
1141.1753	1275.2530		1290.2683	
1412.2561	1427.6568		1479.2988	
1482.3901	1491.6421		1511.4886	
1585.6132	1799.3026		3073.0908	
3081.7636	3133.5153		3140.5555	
3188.8895	3198.1217		3261.3845	
Zero-point correction (Hartree): 0.101870				

acetone

E(RM052X/Aug-CC-pVTZ) (Hartree): -193.20114139
 E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -192.67624545
 E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -192.85142020
 E(ROHF-UCCSD(T)/Aug-CC-pVQZ) (Hartree): -192.90077444
 Electronic state : 1-A
 Cartesian coordinates (Angs):

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C	1.279324	-0.610205	-0.000027	
C	-1.279324	-0.610205	0.000238	
H	1.307911	-1.260599	-0.872756	
H	2.129588	0.060941	-0.005558	
H	1.312643	-1.251168	0.879545	
H	-1.312636	-1.251485	-0.879102	
H	-1.307917	-1.260283	0.873202	
H	-2.129588	0.060943	0.005522	
O	0.000000	1.389929	-0.000241	
Rotational constants (GHz):	10.2514900	8.6482500	4.9768600	
Vibrational harmonic frequencies (cm-1):				
42.8105	144.8107		380.0086	
495.6686	542.5237		812.8773	
898.3009	905.4888		1097.4285	
1140.4615	1265.6303		1405.1037	
1414.1466	1478.8309		1486.7642	
1489.7020	1510.4260		1840.2737	
3093.9009	3099.8350		3148.4869	
3155.7407	3209.9939		3211.0343	
Zero-point correction (Hartree): 0.084908				

CH3COHOCH3.pm

E(UM052X/Aug-CC-pVTZ) (Hartree): -344.17632082
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.30538282
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.60507528
Electronic state : 2-A
Cartesian coordinates (Angs):
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C -0.366908 0.028118 0.062589
O -0.199577 -0.141192 1.423230
H 0.626013 0.286592 1.675337
O 1.908436 -0.179666 -0.133034
C -1.553134 -0.772981 -0.395034
H -2.453066 -0.353328 0.043673
H -1.629905 -0.738925 -1.477539
H -1.440840 -1.801498 -0.067604
C -0.396000 1.482156 -0.347385
H -0.490846 1.571141 -1.425782
H -1.243429 1.962952 0.131983
H 0.522080 1.970735 -0.030717
Rotational constants (GHz): 4.8819300 3.0820100 2.9943000
Vibrational harmonic frequencies (cm-1):
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285.9003 343.0259 393.0081
421.6523 465.6799 506.3466
616.1965 764.0881 858.7239
951.2168 1021.0689 1033.1092
1144.9429 1205.9669 1284.1275
1302.4550 1395.1191 1432.5731
1457.2162 1499.2282 1503.4050
1521.7081 1524.6965 3091.4298
3100.6293 3166.3911 3177.4477
3180.4060 3183.3135 3823.8111
Zero-point correction (Hartree): 0.105409

CH3COHOCH3.pp

E(UM052X/Aug-CC-pVTZ) (Hartree): -344.17258043
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.30179447
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.60143331
Electronic state : 2-A
Cartesian coordinates (Angs):
O -0.816631 -0.658560 -0.521603
C 0.353484 0.043322 0.051844
O 0.335787 -0.112829 1.430492
O -1.940485 -0.165457 -0.103032
H 0.472324 -1.038419 1.650528
C 1.521420 -0.653935 -0.603106
H 1.478251 -0.533614 -1.681322
H 2.444173 -0.222957 -0.227397
H 1.499358 -1.716986 -0.370454
C 0.254186 1.512684 -0.256062
H 1.143294 2.008474 0.121431
H 0.181022 1.663839 -1.328738
H -0.622337 1.922010 0.233036
Rotational constants (GHz): 4.8192400 3.0723400 2.9652900
Vibrational harmonic frequencies (cm-1):
130.9135 202.2131 246.9310
282.9682 325.1755 367.5031
405.6657 431.2168 493.8945
614.1494 772.8279 861.5291
954.9239 1021.0471 1028.4181
1152.6721 1193.3813 1262.2179
1300.4323 1384.2167 1436.8596
1445.1779 1498.6002 1501.8423
1515.9012 1523.6482 3089.8284
3098.8054 3162.4715 3173.1275
3184.6791 3187.3329 3854.0366
Zero-point correction (Hartree): 0.105034

CH3COHOCH3.pt

E(UM052X/Aug-CC-pVTZ) (Hartree): -344.17356680
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.30256884
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.60248128
Electronic state : 2-A
Cartesian coordinates (Angs):

O	0.883078	-0.070758	-0.781894	
C	-0.382806	0.010354	-0.005343	
O	-1.370504	-0.070096	-0.972921	
O	1.929498	-0.005606	-0.023477	
H	-1.398972	-0.961960	-1.329634	
C	-0.406807	-1.149260	0.959996	
H	0.422134	-1.074496	1.655303	
H	-1.345281	-1.130134	1.506027	
H	-0.325459	-2.088507	0.415510	
C	-0.453798	1.365518	0.643416	
H	-0.435662	2.131657	-0.125531	
H	-1.381779	1.440499	1.202386	
H	0.388909	1.494948	1.313857	
Rotational constants (GHz):				4.7675100 3.0559800 2.9801900
Vibrational harmonic frequencies (cm-1):				
137.4652	213.7186		256.6103	
279.7465	354.7439		365.9677	
372.8861	473.4393		497.1830	
548.7479	772.2001		883.0949	
957.3060	1019.2804		1037.2043	
1150.0301	1191.2230		1285.4872	
1319.7774	1383.0802		1432.8269	
1444.3896	1496.8361		1503.8181	
1519.4121	1526.1058		3086.6734	
3095.5733	3159.9895		3173.4726	
3183.2220	3188.7248		3860.8620	
Zero-point correction (Hartree): 0.105186				
HO2				

E(UM052X/Aug-CC-pVTZ) (Hartree): -150.94420033				
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -150.59977968				
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -150.72605502				
E(ROHF-UCCSD(T)/Aug-CC-pVQZ) (Hartree): -150.76505290				
Point group : CS				
Electronic state : 2-A"				
Cartesian coordinates (Angs):				
O	0.054932	0.708542	0.000000	
O	0.054932	-0.600610	0.000000	
H	-0.878913	-0.863457	0.000000	
Rotational constants (GHz):				630.9298100 34.6623400 32.8572100
Vibrational harmonic frequencies (cm-1):				
1240.8792 (A')	1469.2622 (A')		3707.9570 (A')	
Zero-point correction (Hartree): 0.014622				
TSa				

E(UM052X/Aug-CC-pVTZ) (Hartree): -344.15409159				
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.28170359				
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.58214724				
Electronic state : 2-A				
Cartesian coordinates (Angs):				
C	0.563064	0.000000	0.216766	
O	-0.049910	0.000000	1.332613	
O	-1.026930	0.000000	-0.900037	
O	-1.934592	0.000000	-0.007381	
H	-1.235397	0.000000	0.926536	
C	1.165510	-1.280475	-0.277791	
H	1.311294	-1.257873	-1.353233	
H	2.136270	-1.399632	0.203007	
H	0.533613	-2.116179	0.002630	
C	1.165509	1.280475	-0.277791	
H	2.136270	1.399633	0.203007	
H	1.311294	1.257873	-1.353233	
H	0.533613	2.116179	0.002630	
Rotational constants (GHz):				4.8724400 2.8736800 2.7590200
Vibrational harmonic frequencies (cm-1):				
i628.2509	113.2629		185.2937	
214.9113	268.4959		286.1844	
387.5183	526.6448		615.7914	
706.8581	752.2749		851.0191	
924.0118	983.7890		1053.3549	
1089.0960	1160.7170		1294.1090	
1368.1140	1421.4357		1428.7960	
1488.3980	1490.7599		1493.7654	
1513.8953	1664.2139		1928.9970	
3088.6523	3092.7934		3156.0317	
3161.4227	3193.0952		3195.3246	

Zero-point correction (Hartree): 0.100465

b) B3LYP/cc-pVTZ geometries

The geometries were obtained from the supporting information provided by Hermans et al.²

acetone..HO2.a

E(UB3LYP/CC-pVTZ) (Hartree): -344.21978692
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.29709874
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.59696895
Electronic state : 2-A
Cartesian coordinates (Angs):
C -1.154293 -0.066269 0.007335
O -0.336057 -0.970369 0.018353
H 1.373182 -0.818403 0.038825
O 2.363716 -0.714839 0.040823
O 2.574152 0.590548 -0.071834
C -0.749176 1.382232 0.040466
H -1.068745 1.818956 0.990529
H 0.328713 1.485246 -0.061456
H -1.262821 1.938619 -0.745853
C -2.628313 -0.375355 -0.038226
H -3.157834 0.160967 0.751210
H -3.042619 -0.027031 -0.987478
H -2.793674 -1.444721 0.058029
Rotational constants (GHz): 7.3478100 1.4993400 1.2655800
Vibrational harmonic frequencies (cm-1):
24.1126 59.9543 83.3091
106.4376 142.6707 157.3456
235.1780 396.9073 495.1318
560.2946 704.3795 799.4189
894.2767 910.5423 1097.8856
1126.6794 1199.0519 1259.5513
1394.0529 1402.0477 1461.0990
1466.7218 1473.3577 1493.0268
1574.9425 1755.5963 3024.8939
3035.2664 3080.1322 3089.0724
3132.2525 3145.0496 3240.5745
Zero-point correction (Hartree): 0.100288

acetone

E(RB3LYP/CC-pVTZ) (Hartree): -193.23315782
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -192.67726506
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -192.85172202
Point group : C2V
Electronic state : 1-A1
Cartesian coordinates (Angs):
C 0.000000 0.000000 0.184854
C 0.000000 1.288132 -0.611596
C 0.000000 -1.288132 -0.611596
H -0.876879 1.331865 -1.261519
H 0.000000 2.140866 0.061926
H 0.876879 1.331865 -1.261519
H -0.876879 -1.331865 -1.261519
H 0.876879 -1.331865 -1.261519
H 0.000000 -2.140866 0.061926
O 0.000000 0.000000 1.394032
Rotational constants (GHz): 10.1924200 8.5207100 4.9211100
Vibrational harmonic frequencies (cm-1):
18.7053 132.8217 377.9300
489.6186 535.2593 781.7587
884.7872 885.6786 1084.3873
1120.4172 1233.8576 1386.8630
1387.5347 1460.5097 1465.9615
1470.4680 1488.1311 1794.2096
3026.0070 3033.1576 3077.9625
3085.4881 3139.1723 3140.2610
Zero-point correction (Hartree): 0.083155

CH3COHOCH3.pm

E(UB3LYP/CC-pVTZ) (Hartree): -344.21918700
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.30704282
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.60556499

Electronic state : 2-A
 Cartesian coordinates (Angs):

O	0.813880	-0.531251	-0.687096
C	-0.380832	0.028328	0.069852
O	-0.167414	-0.157073	1.420654
H	0.690386	0.238034	1.632018
O	1.938468	-0.164382	-0.124598
C	-1.538143	-0.831160	-0.379844
H	-2.458495	-0.464463	0.072099
H	-1.639661	-0.798103	-1.463189
H	-1.376425	-1.859539	-0.063416
C	-0.478708	1.492924	-0.324298
H	-0.615438	1.601997	-1.399360
H	-1.325352	1.945993	0.189613
H	0.431614	2.017182	-0.033700

Rotational constants (GHz): 4.8192000 3.0227300 2.9280700
 Vibrational harmonic frequencies (cm-1):

104.9642	192.9858	253.1076
273.4942	335.9886	365.9334
410.7507	444.4026	491.1278
589.1794	687.6626	820.3942
938.8709	1005.7079	1020.3347
1119.6214	1177.4092	1219.8171
1271.5851	1389.7148	1410.8456
1434.5210	1479.8604	1483.9932
1500.9323	1504.2952	3043.6508
3055.6865	3115.1674	3119.6762
3127.8776	3134.1102	3737.8938

Zero-point correction (Hartree): 0.103113

CH3COHOCH3.pp

 E(UB3LYP/CC-pVTZ) (Hartree): -344.21549298
 E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.30348307
 E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.60198624
 Electronic state : 2-A
 Cartesian coordinates (Angs):

O	-0.833499	-0.680941	-0.491989
C	0.366060	0.048547	0.053701
O	0.355879	-0.044875	1.439009
O	-1.972975	-0.166304	-0.089227
H	0.492552	-0.963372	1.698198
C	1.520775	-0.699587	-0.587870
H	1.470334	-0.638322	-1.673644
H	2.461255	-0.266418	-0.251698
H	1.496155	-1.753105	-0.304264
C	0.269860	1.510562	-0.319001
H	1.141990	2.037072	0.065012
H	0.229150	1.627135	-1.400397
H	-0.626853	1.936839	0.123480

Rotational constants (GHz): 4.7520700 3.0126200 2.8943700
 Vibrational harmonic frequencies (cm-1):

111.5311	191.8008	230.2472
270.9602	321.3484	369.2922
397.6817	425.6512	479.5531
591.4427	705.3184	819.2486
939.8664	1000.0276	1016.4886
1131.4110	1165.2558	1200.4102
1267.8221	1380.3602	1416.4805
1422.8207	1480.8611	1484.1996
1496.3113	1504.3937	3041.0938
3058.4806	3108.2254	3124.4691
3130.5794	3143.7530	3790.0585

Zero-point correction (Hartree): 0.103013

CH3COHOCH3.pt

 E(UB3LYP/CC-pVTZ) (Hartree): -344.21651955
 E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.30428668
 E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.60306535
 Electronic state : 2-A
 Cartesian coordinates (Angs):

O	0.901327	-0.048432	-0.778640
C	-0.397597	0.007812	-0.003816
O	-1.366304	-0.055257	-0.993204
O	1.963742	0.002210	-0.009968
H	-1.395073	-0.947770	-1.356216
C	-0.419316	-1.180262	0.938421

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H      0.420803      -1.135177      1.627405
H      -1.350028      -1.177385      1.503843
H      -0.351502      -2.112386      0.374263
C      -0.482286      1.359154      0.668256
H      -0.491617      2.141681      -0.088243
H      -1.400036      1.421475      1.251094
H      0.372529      1.501168      1.325184
Rotational constants (GHz):    4.7035700    2.9896700    2.9102300
Vibrational harmonic frequencies (cm-1):
127.6577      208.8278      248.3443
270.2040      347.8923      359.3209
375.4125      459.2398      488.5697
522.7270      722.6399      829.5449
942.1703      1007.6976     1018.3438
1131.9337     1154.4035     1205.6416
1287.1005     1378.3770     1412.0353
1422.5345     1478.2605     1486.2531
1499.7445     1507.0356     3039.4897
3056.2766     3107.7036     3125.9679
3136.0872     3141.9348     3792.6705
Zero-point correction (Hartree): 0.103183

HO2
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E(UB3LYP/CC-pVTZ) (Hartree): -150.96848020
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -150.60066603
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -150.72660766
E(ROHF-UCCSD(T)/Aug-CC-pVQZ) (Hartree): -150.76537056
Point group : CS
Electronic state : 2-A"
Cartesian coordinates (Angs):
O      0.055350      0.718742      0.000000
O      0.055350      -0.610515     0.000000
H      -0.885607     -0.865819     0.000000
Rotational constants (GHz):    620.4772900    33.6732400    31.9398600
Vibrational harmonic frequencies (cm-1):
1160.0435 ( A')      1431.6074 ( A')      3605.0039 ( A')
Zero-point correction (Hartree): 0.014117

TSa
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E(UB3LYP/CC-pVTZ) (Hartree): -344.20387632
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.28309106
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.58232018
Electronic state : 2-A
Cartesian coordinates (Angs):
C      0.583472      0.000000      0.212002
O      -0.052606     -0.000003      1.324450
O      -1.070936     -0.000001     -0.915761
O      -1.963719      0.000000      0.012973
H      -1.186805     -0.000001      0.961081
C      1.187977     -1.287826     -0.276311
H      1.341443     -1.280235     -1.354114
H      2.163046     -1.414650      0.203343
H      0.559708     -2.129501      0.005428
C      1.187971      1.287831     -0.276308
H      2.163035      1.414662      0.203352
H      1.341443      1.280240     -1.354110
H      0.559694      2.129501      0.005427
Rotational constants (GHz):    4.8299900    2.7898100    2.6728000
Vibrational harmonic frequencies (cm-1):
i824.6655      103.7719      162.4068
193.1827      248.8764      262.4804
377.5132      513.3527      530.2537
609.1317      731.0742      816.6889
908.9457      962.0615     1012.4920
1074.0469     1131.5601     1260.9410
1287.2751     1402.8543     1405.3228
1465.7341     1467.5952     1470.1822
1490.6052     1590.8054     1867.3679
3025.1773     3030.3544     3093.5671
3098.8674     3135.9002     3138.7398
Zero-point correction (Hartree): 0.097663

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c) MP2/6-311G(d,p) geometries

It is assumed that these geometries are very similar to those obtained by Cours et al.³

acetone..HO2.a

E(MP2/6-311G(d,p)) (Hartree): -343.25249079
E(PMP2/6-311G(d,p)) (Hartree): -343.25024023
E(PUHF/6-311G(d,p)) (Hartree): -342.24095284
E(UHF/6-311G(d,p)) (Hartree): -342.24300381
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.29640790
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.59617417
Electronic state : 2-A
Cartesian coordinates (Angs):
C -1.157681 -0.071982 0.010601
O -0.333168 -0.977464 0.027319
H 1.409419 -0.809330 0.077698
O 2.386210 -0.689161 0.089632
O 2.570571 0.578821 -0.145894
C -0.766214 1.384341 0.080675
H -0.996016 1.753156 1.086818
H 0.299444 1.506022 -0.113213
H -1.359750 1.972572 -0.624404
C -2.634272 -0.378544 -0.071610
H -3.186934 0.204831 0.670207
H -3.002633 -0.082835 -1.059792
H -2.803427 -1.444882 0.076234
Rotational constants (GHz): 7.3421500 1.4865700 1.2597400
Vibrational harmonic frequencies (cm-1):
36.3103 57.4082 102.1431
127.2322 141.1390 148.8962
224.4670 392.1022 483.7271
554.6295 688.0193 816.4790
899.9372 929.7875 1103.3252
1125.5749 1277.1661 1325.3393
1404.2438 1416.9644 1482.5497
1486.0532 1494.9277 1513.9836
1591.8264 1770.7476 3076.4760
3082.2163 3160.7899 3165.9196
3210.0216 3210.4887 3470.6268
Zero-point correction (Hartree): 0.102453

acetone

E(MP2/6-311G(d,p)) (Hartree): -192.64797184
E(RHF/6-311G(d,p)) (Hartree): -192.01133627
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -192.67795416
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -192.85181362
Electronic state : 1-A
Cartesian coordinates (Angs):
C 0.000000 0.186975 0.000000
C -1.286576 -0.617677 0.002369
C 1.286575 -0.617678 -0.002369
H -1.258490 -1.386332 0.780487
H -2.136138 0.047362 0.158451
H -1.395583 -1.130105 -0.959455
H 1.395587 -1.130099 0.959458
H 1.258486 -1.386338 -0.780482
H 2.136137 0.047359 -0.158460
O 0.000001 1.403554 0.000000
Rotational constants (GHz): 10.0553100 8.5402000 4.8985900
Vibrational harmonic frequencies (cm-1):
81.1628 138.7485 376.6758
481.3098 534.3786 803.4352
889.2178 906.2359 1091.3165
1121.1721 1253.8614 1395.4238
1405.8426 1482.3668 1486.2198
1491.6076 1506.8279 1787.6709
3075.2468 3079.9838 3158.2337
3163.1039 3204.2506 3205.3840
Zero-point correction (Hartree): 0.084565

CH3COHOCH3.pm

E(MP2/6-311G(d,p)) (Hartree): -343.25820354
E(PMP2/6-311G(d,p)) (Hartree): -343.25557139
E(PUHF/6-311G(d,p)) (Hartree): -342.23865799
E(UHF/6-311G(d,p)) (Hartree): -342.24103052
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.30628106
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.60515946
Electronic state : 2-A

Cartesian coordinates (Angs):

O	0.798269	-0.603705	-0.628442
C	-0.365698	0.031881	0.061701
O	-0.218047	-0.118230	1.427800
H	0.601387	0.336414	1.655383
O	1.909483	-0.191189	-0.117067
C	-1.549455	-0.786058	-0.392425
H	-2.462758	-0.361768	0.029198
H	-1.615995	-0.779880	-1.482154
H	-1.432741	-1.811924	-0.038668
C	-0.389128	1.486541	-0.370969
H	-0.482822	1.564514	-1.456321
H	-1.235504	1.985278	0.106037
H	0.536479	1.978174	-0.061650

Rotational constants (GHz): 4.8367100 3.0769600 2.9790400

Vibrational harmonic frequencies (cm-1):

126.6778	188.6101	277.4151
281.3328	343.2504	379.3878
419.3095	443.5107	507.7290
620.8358	762.7756	862.7960
956.3782	1017.1429	1034.5507
1154.9636	1215.7108	1298.6037
1331.3208	1399.6738	1427.0717
1461.8326	1497.2322	1503.2089
1521.0476	1525.5120	3088.8474
3098.0108	3187.9947	3192.5906
3200.6657	3202.0198	3847.3285

Zero-point correction (Hartree): 0.105651

CH3COHOCH3.pp

E(MP2/6-311G(d,p)) (Hartree): -343.25505934
 E(PMP2/6-311G(d,p)) (Hartree): -343.25526992
 E(PUHF/6-311G(d,p)) (Hartree): -342.24085786
 E(UHF/6-311G(d,p)) (Hartree): -342.24065321
 E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.30287446
 E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.60168759

Electronic state : 2-A

Cartesian coordinates (Angs):

O	-0.818712	-0.686359	-0.486939
C	0.350797	0.046176	0.050272
O	0.355599	-0.038728	1.436779
O	-1.945878	-0.178390	-0.087463
H	0.508007	-0.961524	1.664254
C	1.517001	-0.685076	-0.586325
H	1.481704	-0.603993	-1.674514
H	2.448860	-0.251385	-0.218633
H	1.485506	-1.745342	-0.316309
C	0.245905	1.507607	-0.320406
H	1.137121	2.029902	0.032999
H	0.165174	1.613859	-1.403874
H	-0.636669	1.934061	0.155821

Rotational constants (GHz): 4.7815100 3.0650300 2.9433600

Vibrational harmonic frequencies (cm-1):

126.8977	210.3841	259.1534
286.2897	336.0838	386.4411
419.9500	433.4826	498.8899
620.4266	775.4435	869.3244
956.5451	1021.0255	1026.2001
1169.8165	1200.4270	1264.3853
1305.1941	1393.2663	1432.9035
1450.9496	1497.2536	1503.8040
1516.3274	1524.8989	3084.6641
3101.6047	3177.5470	3196.1935
3201.6052	3215.3240	3867.3386

Zero-point correction (Hartree): 0.105548

CH3COHOCH3.pt

E(MP2/6-311G(d,p)) (Hartree): -343.25570802
 E(PMP2/6-311G(d,p)) (Hartree): -343.25449473
 E(PUHF/6-311G(d,p)) (Hartree): -342.23781873
 E(UHF/6-311G(d,p)) (Hartree): -342.23896078
 E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.30347952
 E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.60260978

Electronic state : 2-A

Cartesian coordinates (Angs):

O	0.889921	-0.045915	-0.779515
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C	-0.383277	0.008306	-0.005975
O	-1.366727	-0.051112	-0.980304
O	1.932622	0.003074	-0.015972
H	-1.366238	-0.946458	-1.333403
C	-0.405570	-1.182277	0.931889
H	0.414113	-1.122216	1.647790
H	-1.360186	-1.199019	1.462000
H	-0.298386	-2.107439	0.356347
C	-0.469880	1.355218	0.671664
H	-0.449838	2.135657	-0.091465
H	-1.406796	1.420007	1.228826
H	0.373170	1.483617	1.350767
Rotational constants (GHz): 4.7369700 3.0501700 2.9602200			
Vibrational harmonic frequencies (cm-1):			
139.6752	227.6163	276.3880	
281.9739	362.8107	370.0655	
381.6035	478.4310	499.7908	
552.8900	769.6509	895.0652	
956.8133	1017.8523	1040.3449	
1167.7543	1195.4347	1314.6683	
1326.8785	1392.4488	1427.0817	
1450.4453	1494.3030	1506.2460	
1518.7576	1525.7392	3084.4757	
3099.4063	3177.6863	3197.0242	
3209.4217	3213.9591	3869.7092	
Zero-point correction (Hartree): 0.105758			
HO2			

E(MP2/6-311G(d,p)) (Hartree): -150.58562573			
E(PMP2/6-311G(d,p)) (Hartree): -150.58575053			
E(PUHF/6-311G(d,p)) (Hartree): -150.22876738			
E(UHF/6-311G(d,p)) (Hartree): -150.21815617			
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -150.59979291			
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -150.72607396			
E(ROHF-UCCSD(T)/Aug-CC-pVQZ) (Hartree): -150.76507326			
Point group : CS			
Electronic state : 2-A"			
Cartesian coordinates (Angs):			
O	0.055112	0.707966	0.000000
O	0.055112	-0.601638	0.000000
H	-0.881790	-0.850623	0.000000
Rotational constants (GHz): 625.7031900 34.7001900 32.8769000			
Vibrational harmonic frequencies (cm-1):			
1245.4808 (A')	1460.1293 (A')	3736.5745 (A')	
Zero-point correction (Hartree): 0.014676			
TSa			

E(MP2/6-311G(d,p)) (Hartree): -343.23906838			
E(PMP2/6-311G(d,p)) (Hartree): -343.23757234			
E(PUHF/6-311G(d,p)) (Hartree): -342.19707730			
E(UHF/6-311G(d,p)) (Hartree): -342.19887450			
E(ROHF-UCCSD(T)/Aug-CC-pVDZ) (Hartree): -343.28294401			
E(ROHF-UCCSD(T)/Aug-CC-pVTZ) (Hartree): -343.58258185			
Electronic state : 2-A			
Cartesian coordinates (Angs):			
C	-0.583181	0.000000	0.230253
O	0.025962	0.000000	1.339362
O	1.072493	0.000000	-0.907590
O	1.938671	0.000000	0.018795
H	1.260811	0.000000	0.894946
C	-1.173158	1.287363	-0.289302
H	-1.275985	1.270704	-1.375991
H	-2.167392	1.412579	0.154940
H	-0.547045	2.126724	0.016366
C	-1.173158	-1.287363	-0.289302
H	-2.167392	-1.412579	0.154940
H	-1.275985	-1.270704	-1.375991
H	-0.547045	-2.126724	0.016366
Rotational constants (GHz): 4.8069200 2.8190400 2.7101700			
Vibrational harmonic frequencies (cm-1):			
i739.6011	113.3297	177.6714	
224.6494	253.8280	272.6015	
381.5440	525.4329	599.5356	
628.9574	830.6925	917.1663	
944.2011	967.6607	1038.4168	
1089.3201	1196.1901	1288.5844	

1410.7207	1421.2476	1484.3333
1487.7291	1491.2681	1505.8622
1629.4178	1720.9232	1944.6962
3076.5809	3080.2239	3166.2807
3170.3578	3201.5703	3204.7693

Zero-point correction (Hartree): 0.101255