

SUPPORTING INFORMATION

DEC. 24, 2018

Kinetics of the Strongly Correlated CH₃O + O₂ Reaction: The Importance of Quadruple Excitations in Atmospheric and Combustion ChemistryBo Long,^{a,b,*} Junwei Lucas Bao,^b and Donald G. Truhlar^b.^aCollege of Materials Science and Engineering, Guizhou Minzu University, Guiyang, 550025, China^bDepartment of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, USA

*email: wwwltcommon@sina.com (Bo Long), truhlar@umn.edu (Donald G. Truhlar)

Contents

Note on spin-orbit coupling	S-3
Note on units	S-3
Orbitals for CC, QCI, and density functional calculations	S-3
Coupled cluster abbreviations	S-3
Detailed explanations of W2X, MW2-F12, MW3X-L, and W3X-L	S-4
Electronic partition functions and symmetry numbers	S-4
Geometry optimization and scale factors for vibrational frequencies	S-5
Pre-reactive complex	S-5
Table S1. The activation enthalpies at 0 K and barrier heights) for TS1 and TS2	S-6
Table S2. References for basis sets and number of contracted basis functions for transition state calculations	S-7
Table S3. Selected internuclear distances of TS1	S-8
Table S4. Selected bond angles of TS1	S-9
Table S5. Components of barrier height increments (kcal/mol) for TS1	S-10
Table S6. The components of GMM(P)	S-11
Table S7. Frequencies and zero-point vibrational energies of CH ₃ O	S-12
Table S8. The T1, D1, and T1/D1 diagnostics values of CH ₃ O, O ₂ , and TS1	S-13
Table S9. Frequencies and zero-point vibrational energies of O ₂	S-14
Table S10. Frequencies and zero-point vibrational energies of TS1	S-15
Table S11. The scale factors for the vibrational frequencies	S-16
Table S12. Rate constants, transmission coefficients and activation energies	S-17

To whom correspondence should be addressed. E-mail: wwwltcommon@sina.com (Bo Long), truhlar@umn.edu (Donald G. Truhlar)

Table S13.Coordinates and absolute energies of optimized structures	S-19
CH ₃ O input for MW2-F12 in Molpro code	S-22
References	S-26

Note on spin-orbit coupling

All calculations included in the entire article and the entire SI include spin-orbit coupling (for which we use the ground-state splitting measured by Foster et al.¹), which raises the barrier height, enthalpy of activation, and reaction energy by 0.09 kcal/mol.

Note on units

In the entire article and SI, except for table S10, all energies and enthalpies are in kcal/mol, all frequencies are in cm^{-1} , all coordinates are in Å and deg, and all rate constants are in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In Table S13, energies are in hartrees and coordinates are in Å.

Orbitals for CC, QCI, and density functional calculations

All coupled cluster (CC) and quadratic configuration interaction (QCI) calculations are unrestricted in the post-SCF steps, but some of them are based on unrestricted Hartree–Fock (UHF) orbitals and some are based on restricted open-shell Hartree–Fock (ROHF) orbitals or, for singlets, on restricted Hartree–Fock (RHF) orbitals. The former are denoted CC or QCI, and the latter are denoted RCC or RQCI. The W2X, W3X-L, MW-F12, and all F12a calculations with *Molpro* are RCC. The T–(T) term is also RCC. The (Q)–T, Q–(Q), and (P)–Q used in GMM(P) are calculated with MRCC and are CC.

All density functional calculations are spin-polarized (i.e., unrestricted; i.e., different orbitals for different spins).

Coupled cluster abbreviations

As mentioned above, coupled cluster calculations based on ROHF orbitals are denoted RCC, i.e., with a prefix R before CC, and coupled cluster calculations based on UHF orbitals are simply denoted CC. The letters after CC denotes the excitation levels included. In order of increasing completeness, we have:

RCCSD	single and double excitations
RCCSD(T)	single and double excitations and noniterative triple excitations
RCCSDT or CCSDT	single, double, and triple excitations
CCSDT(Q)	single, double, and triple excitations and noniterative quadruple excitations
CCSDTQ	single, double, triple, and quadruple excitations
CCSDTQ(P)	single, double, triple, and quadruple excitations and noniterative pentuple excitations

Detailed explanations of W2X, MW2-F12, MW3X-L, and W3X-L

The W2X procedure provides a cost-efficient approximation to the CCSD(T)/CBS energy; the W3X-L procedure provides a cost-efficient approximation to the CCSDT(Q)/CBS energy. These methods were introduced by Chan and Radom.² We³ have given the label MW-F12 to the method that was used by Sylvestry et al.⁴ to calculate the single-point CCSD(T)/CBS energy of benzene in the recently proposed W4-F12 approach. It is a larger-basis set alternative to W2X, and it is explained in detail in the SI of a previous paper.³ MW3X-L is a new method introduced here that combines MW2-F12 with post-CCSD(T) calculations from W3X-L.

Electronic partition functions and symmetry numbers

The rate constants include the ratio of electronic partition functions $\frac{g_{\text{TS1}}}{g_{\text{CH}_3\text{O}}g_{\text{O}_2}}$.

For the purpose of computing electronic and rotational partition functions, we describe CH₃O as a doublet E state perturbed by Jahn-Teller vibronic coupling and by spin-orbit coupling. The splitting between the two vibronically split states was estimated to be 0.18 kcal/mol, based on the work of Foster et al.¹ This treatment yields

$$g_{\text{TS1}} = 2$$

$$g_{\text{CH}_3\text{O}} \approx 2 + 2 \exp\left[-(0.18 \text{ kcal/mol}) / RT\right]$$

$$g_{\text{O}_2} \approx 3$$

with a symmetry number of 3 for the CH₃O rotational partition function. The symmetry numbers for the other rotational partition functions are 2 for O₂ and 1 for TS1.

Geometry optimization and scale factors for vibrational frequencies

Reactant geometries and energies of reactants were calculated in separate runs for the two species except for CASPT2 where the reactants were optimized in separate runs and energies of reactants were done as a supermolecule. The vibrational frequencies for any given line in Table 1 or S12 are computed by the method used to optimize the geometry for that line. These are the unscaled values. Then we used the quasiharmonic approximation for calculating vibrational zero point energies and vibrational contributions to enthalpies, partition functions, and free energies. The quasiharmonic approximation involves using harmonic oscillator formulas but with scaled frequencies. The frequencies are scaled to account for both systematic errors in a given electronic structure method and also to account for anharmonicity. For all methods in Tables 1, S6-S7, and S9-S10 except CASPT2, the scaling factors were obtained by a standard method⁵ for obtaining a scaling factor optimized for zero point energies. For CASPT2, we scaled the vibrational frequencies (and hence also the zero point energies) by using the experimental zero-point vibrational energies (22.6^{6,7} and 2.28⁸ kcal/mol) of CH₃O and O₂. See Table S11 for a compilation of the scale factors.

Pre-reactive complex

We did not consider the effect of the pre-reactive complex on the CH₃ + O₂ reaction. In general the main possible effect of such a complex is to increase the tunneling probability. This possible effect can become important when there is significant population of complex energy levels at lower energy than the ground-state energy of the bimolecular reactants. In the present case, the binding energy of the complex is small⁹ ($\lesssim 1$ kcal/mol), so the effect of the pre-reactive complex is not expected to be large at the temperatures ($T > 250$ K) considered in this article.

Table S1. The activation enthalpies at 0 K ($\Delta H_0^\ddagger$ in kcal/mol) and barrier heights ($\Delta V^\ddagger$ in kcal/mol) for the $\text{CH}_3\text{O} + \text{O}_2$ reaction.^a

Method	TS1 ($C_s, {}^2A''$) ^a		TS2 ($C_s, {}^2A''$) ^a	
	$\Delta H_0^\ddagger$	$\Delta V^\ddagger$	$\Delta H_0^\ddagger$	$\Delta V^\ddagger$
W3X-L//RCCSD(T)-F12a/jun-cc-pVTZ	2.57	2.27	10.06	11.53
W3X-L//RCCSD(T)-F12a/cc-pVDZ-F12	2.37	2.29	9.66	11.39
MW2-F12//RCCSD(T)-F12a/jun-cc-pVTZ	4.83	4.53	14.36	15.65
W2X//RCCSD(T)-F12a/jun-cc-pVTZ	4.32	4.02	13.66	14.95

^aThe transition states TS1 and TS2 are doublet systems with C_s symmetry. All reactant energies used to compute barrier heights and reaction energies in the article and the SI include a spin-orbit contribution of -0.09 kcal/mol, and this raised all reported barrier heights and reaction energies by 0.09 kcal/mol. (Exception: Absolute energies in hartrees in Table S11 do not include spin-orbit coupling.)

Table S2. References for basis sets and the number of contracted basis functions for the transition state calculation with each choice of basis set

Basis set	Reference	Number
cc-pVTZ-F12	10	266
jun-cc-pVTZ	11	198
maug-cc-pVTZ	12	180
MG3S ^a	13,14	163
cc-pVTZ	15	162
cc-pVDZ-F12	10	147
jun-cc-pVDZ	11	87
cc-pVDZ	15	71
VDZ(d) ^b	16	62
cc-VDZ ^c	2	42

^aFor H, C, and O, MG3S is the same as 6-311+G(2df,2p).

^bVDZ(d) is defined in ref. 16 as cc-pVDZ with no polarization functions on hydrogens.

^ccc-VDZ is defined in ref. 2 as cc-pVDZ with no polarization functions on any atom; it is also called cc-pVDZ(NP).

Table S3. Selected internuclear distances of TS1 (Å) and their mean unsigned deviation (MUD) from the first row. The coordinates are defined in Fig. 1.

	R ₁	R ₂	R ₃	MUD
RCCSD(T)-F12a/cc-pVTZ-F12 ^{a,b}	1.270	1.377	2.092	0.000
RCCSD(T)-F12a/jun-cc-pVTZ ^a	1.268	1.380	2.094	0.002
RCCSD(T)-F12a/cc-pVDZ-F12 ^a	1.271	1.377	2.100	0.003
RQCISD/MG3S ^c	1.220	1.461	2.002	0.075
QCISD/MG3S ^d	1.284	1.356	2.347	0.097
CASPT2(11,9)/aug-cc-pVTZ	1.282	1.363	2.155	0.030
MN15-L/maug-cc-pVTZ ^e	1.231	1.468	2.090	0.044
MN15-L/MG3S ^e	1.230	1.477	2.111	0.053

^a CCSD(T)-F12a with restricted open-shell Hartree–Fock orbitals

^b This is the best estimate of the transition state geometry.

^c QCISD with restricted open-shell Hartree–Fock orbitals

^d QCISD with unrestricted Hartree–Fock orbitals

^e All density functional calculations are spin-polarized, i.e., unrestricted.

Table S4. Selected bond angles of TS1 (in degrees) and their mean unsigned deviation (MUD) from the first row. The coordinates are defined in Fig. 1. ^a

Method	θ_1	θ_2	θ_3	MUD
RCCSD(T)-F12a/cc-pVTZ-F12 ^b	100.2	140.2	101.3	0.0
RCCSD(T)-F12a/jun-cc-pVTZ	100.3	140.3	101.2	0.1
RCCSD(T)-F12a/cc-pVDZ-F12	100.2	140.5	101.3	0.1
RQCISD/MG3S	101.5	137.0	98.8	2.3
QCISD/MG3S	99.6	148.6	103.0	3.6
CASPT2(11,9)/aug-cc-pVTZ	99.4	142.9	101.6	1.2
MN15-L/maug-cc-pVTZ	103.1	137.3	100.6	2.1
MN15-L/MG3S	102.8	137.2	100.5	2.1

^a See footnotes *a*, *b*, and *c* in Table S3 and as well as the note on orbitals for CC, QCI, and density functional calculations on page S-3. MUD denotes mean unsigned deviation from the best estimate.

^b This is the best estimate of the transition state geometry.

Table S5. Components of barrier height increments (kcal/mol) for TS1.

$E(\text{RCCSDT}) - E[\text{RCCSD}(\text{T})]$	
jun-cc-pVDZ	0.14
jun-cc-pVTZ	0.54
CBS based on jun-cc-pVXZ	0.72*
cc-pVDZ	-0.05
cc-pVTZ	0.40
CBS based on cc-pVXZ	0.59
$E[\text{CCSDT}(\text{Q})] - E(\text{CCSDT})$	
jun-cc-pVDZ	-2.91*
jun-cc-pVTZ	-3.49
CBS based on jun-cc-pVXZ	-3.73
cc-pVDZ	-2.77
cc-pVTZ	-3.38
CBS based on cc-pVXZ	-3.63
$E[\text{CCSDT}(\text{Q})] - E(\text{RCCSD}(\text{T}))$	
CBS based on cc-pVXZ	-3.04
CBS based on jun-cc-pVXZ	-3.01
$E(\text{CCSDTQ}) - E[\text{CCSDT}(\text{Q})]$	
cc-pVDZ	0.60
VDZ(d)	0.59*
$E[\text{CCSDTQ}(\text{P})] - E(\text{CCSDTQ})$	
cc-VDZ	-0.31*

* denotes the method used in GMM(P), GMMQ, and GMM(Q).

Table S6. The components of GMM(P) (in kcal/mol).^a

Method	$DH_0^\ddagger$	$V^\ddagger$
CCSDTQ(P)/cc-VDZ	14.61	14.31
CCSDTQ/cc-VDZ	14.92	14.62
CCSDTQ/VDZ(d)	8.36	8.06
CCSDT(Q)/VDZ(d)	7.77	7.47
CCSDT(Q)/CBS	2.86	2.56
CCSDT/CBS	6.59	6.29
RCCSDT/CBS	5.66	5.36
RCCSD(T)/CBS	4.94	4.64
MW2-F12 ^a	4.83	4.53

^a The geometry for this table is by RCCSD(T)-F12a/jun-cc-pVTZ. All reactant energies used to compute barrier heights and enthalpies in this table (and in Table 1 of the article proper) include a spin-orbit contribution of -0.09 kcal/mol, and this raised all reported barrier heights and enthalpies of activation by 0.09 kcal/mol.

Table S7. Frequencies and zero-point vibrational energies of CH₃O

Method	ZPE ^a (kcal/mol)	ZPE ^b (kcal/mol)	Frequencies (cm ⁻¹) ^c		
RCCSD(T)-F12a/cc-pVTZ-F12	23.07	22.70	3063.7 1511.5 1116.6	3020.8 1391.7 966.5	2938.1 1384.2 747.8
RCCSD(T)-F12a/jun-cc-pVTZ	23.12	22.75	3066.7 1521.9 1118.5	3023.2 1389.7 967.0	2943.2 1384.6 755.7
RCCSD(T)-F12a/cc-pVDZ-F12	23.14	22.74	3065.2 1519.9 1115.8	3022.5 1395.0 968.1	2941.9 1393.3 761.5
CASPT2(11,9)/aug-cc-pVTZ	23.62	22.60	3141.2 1540.1 1113.3	3098.8 1436.2 955.6	3015.5 1415.4 803.3
MN15-L/maug-cc-pVTZ	22.67	22.19	2999.9 1513.9 1138.3	2959.4 1366.9 968.5	2886.9 1366.0 656.8
MN15-L/MG3S	22.66	22.14	3001.0 1513.3 1142.4	2959.6 1366.6 968.5	2885.6 1366.1 648.3
RQCISD/MG3S	23.43	22.94	3098.9 1536.0 1127.5	3048.4 1438.4 984.3	2972.3 1410.5 773.4
QCISD/MG3S	24.02	23.52	3200.5 1711.0 1127.0	3048.2 1534.2 981.7	2969.4 1409.2 818.3

^aUnscaled zero-point energy^bScaled zero-point energy^cUnscaled frequencies

Table S8. The T1, D1, and T1/D1 diagnostics values of CH₃O, O₂, and TS1 by RCCSD(T)/jun-cc-pVTZ

Compound	T1	D1	T1/D1
CH ₃ O	0.021	0.065	0.32
O ₂	0.008	0.015	0.53
TS1	0.034	0.122	0.28

Table S9. Frequencies and zero-point vibrational energies of O₂

Method	ZPE ^a (kcal/mol)	ZPE ^b (kcal/mol)	Frequencies (cm ⁻¹) ^c
RCCSD(T)-F12a/cc-pVTZ-F12	2.29	2.25	1602.6
RCCSD(T)-F12a/jun-cc-pVTZ	2.29	2.25	1601.8
RCCSD(T)-F12a/cc-pVDZ-F12	2.29	2.25	1604.2
CASPT2(11,9)/aug-cc-pVTZ	2.22	2.12	1555.5
MN15-L/maug-cc-pVTZ	2.41	2.36	1683.0
MN15-L/MG3S	2.42	2.36	1694.6
RQCISD/MG3S	2.40	2.35	1678.4
QCISD/MG3S	2.37	2.32	1658.7

^aUnscaled zero-point energy^bScaled zero-point energy^cUnscaled frequencies

Table S10. Frequencies and zero-point vibrational energies of TS1

Method	ZPE ^a (kcal/mol)	ZPE ^b (kcal/mol)	Frequencies (cm ⁻¹) ^c		
RCCSD(T)-F12a/cc-pVTZ-F12	25.70	25.29	3038.5	2956.1	1607.3
			1537.6	1499.6	1372.2
			1252.2	1230.4	1132.9
			687.0	558.8	525.2
			328.9	253.8	1134.5i
RCCSD(T)-F12a/jun-cc-pVTZ	25.71	25.30	3038.8	2956.6	1610.9
			1535.4	1501.9	1372.8
			1255.6	1231.0	1133.3
			688.9	558.6	524.9
			324.6	254.0	1128.8i
RCCSD(T)-F12a/cc-pVDZ-F12	25.51	25.07	3033.7	2951.1	1600.0
			1527.8	1494.6	1366.2
			1246.6	1228.0	1126.3
			678.9	552.9	479.4
			316.2	240.9	1158.9i
CASPT2(11,9)/aug-cc-pVTZ	25.45	24.36	3090.6	2999.2	1585.2
			1522.5	1455.8	1346.4
			1247.0	1229.8	1114.8
			679.9	530.2	490.2
			280.7	230.4	905.1i
MN15-L/maug-cc-pVTZ	25.96	25.41	2946.5	2874.9	1823.4
			1578.3	1520.6	1372.0
			1268.9	1256.4	1107.6
			822.8	585.7	463.7
			282.9	248.8	652.4i
MN15-L/MG3S	25.90	25.33	2945.1	2871.2	1829.2
			1586.5	1519.2	1368.8
			1267.6	1260.1	1099.3
			825.2	579.4	458.6
			265.9	244.0	655.0i
RQCISD/MG3S	26.59	26.03	3088.7	3008.2	1786.4
			1560.0	1472.6	1351.4
			1312.5	1266.3	1182.8
			786.1	610.6	541.3
			362.2	269.0	871.0i
QCISD/MG3S	24.83	24.31	3056.7	2974.7	1582.7
			1501.0	1484.5	1339.7
			1246.6	1222.2	1089.6
			583.5	474.3	444.7
			187.9	182.3	2278.8i

^aUnscaled zero-point energy ^bScaled zero-point energy ^cUnscaled frequencies

Table S11. The scale factors for the vibrational frequencies^a

Method	Scale factor
RCCSD(T)-F12a/cc-pVTZ-F12	0.984
RCCSD(T)-F12a/jun-cc-pVTZ	0.984
RCCSD(T)-F12a/cc-pVDZ-F12	0.983
CASPT2(11,9)/aug-cc-pVTZ	0.957
MN15-L/maug-cc-pVTZ	0.979
MN15-L/MG3S	0.977
RQCISD/MG3S	0.979
QCISD/MG3S	0.979
M11-L/MG3S	0.985
M11-L/maug-cc-pVTZ	0.988

^aSee page S-4 for an explanation of the scaling of vibrational frequencies. Since we use the quasiharmonic approximation, the zero point energies are scaled by the same factor as used for frequencies.

Table S12. Rate constants (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), transmission coefficients (unitless), and activation energies (in kcal/mol) of the $\text{CH}_3\text{O} + \text{O}_2$ reaction

T (K)	k_{HL}^{TST}	κ_{LL}^{SCT}	k_{LL}^{TST}	k_{LL}^{CVT}	Γ_{LL}	k	E_a^g
250	7.56E-16	3.28E+00	1.19E-16	1.06E-16	8.96E-01	1.31E-15	0.58
260	8.76E-16	2.94E+00	1.49E-16	1.35E-16	9.05E-01	1.37E-15	0.63
270	1.01E-15	2.67E+00	1.84E-16	1.67E-16	9.12E-01	1.43E-15	0.69
280	1.15E-15	2.46E+00	2.24E-16	2.06E-16	9.19E-01	1.5E-15	0.74
298	1.42E-15	2.17E+00	3.10E-16	2.88E-16	9.31E-01	1.65E-15	0.85
300	1.45E-15	2.14E+00	3.20E-16	2.99E-16	9.32E-01	1.67E-15	0.87
310	1.62E-15	2.03E+00	3.78E-16	3.54E-16	9.37E-01	1.77E-15	0.93
320	1.80E-15	1.93E+00	4.41E-16	4.16E-16	9.42E-01	1.87E-15	0.99
330	1.99E-15	1.84E+00	5.11E-16	4.84E-16	9.47E-01	1.97E-15	1.06
340	2.19E-15	1.77E+00	5.88E-16	5.60E-16	9.51E-01	2.09E-15	1.12
350	2.40E-15	1.70E+00	6.72E-16	6.42E-16	9.55E-01	2.2E-15	1.19
360	2.62E-15	1.65E+00	7.63E-16	7.32E-16	9.59E-01	2.33E-15	1.26
370	2.85E-15	1.60E+00	8.61E-16	8.29E-16	9.63E-01	2.46E-15	1.32
380	3.09E-15	1.56E+00	9.68E-16	9.34E-16	9.66E-01	2.6E-15	1.39
390	3.34E-15	1.52E+00	1.08E-15	1.05E-15	9.69E-01	2.74E-15	1.46
400	3.60E-15	1.48E+00	1.20E-15	1.17E-15	9.71E-01	2.89E-15	1.53
410	3.87E-15	1.45E+00	1.33E-15	1.30E-15	9.74E-01	3.04E-15	1.6
420	4.16E-15	1.43E+00	1.47E-15	1.44E-15	9.76E-01	3.2E-15	1.67
430	4.45E-15	1.40E+00	1.62E-15	1.58E-15	9.78E-01	3.37E-15	1.74
440	4.75E-15	1.38E+00	1.78E-15	1.74E-15	9.80E-01	3.54E-15	1.81
450	5.07E-15	1.36E+00	1.94E-15	1.91E-15	9.82E-01	3.71E-15	1.88
460	5.40E-15	1.34E+00	2.11E-15	2.08E-15	9.83E-01	3.9E-15	1.94
470	5.73E-15	1.32E+00	2.30E-15	2.26E-15	9.85E-01	4.09E-15	2.01
480	6.08E-15	1.30E+00	2.49E-15	2.46E-15	9.86E-01	4.28E-15	2.08
490	6.45E-15	1.29E+00	2.69E-15	2.66E-15	9.88E-01	4.48E-15	2.15
500	6.82E-15	1.28E+00	2.90E-15	2.87E-15	9.89E-01	4.69E-15	2.22
510	7.21E-15	1.26E+00	3.13E-15	3.09E-15	9.90E-01	4.9E-15	2.28
520	7.60E-15	1.25E+00	3.36E-15	3.33E-15	9.91E-01	5.12E-15	2.35
530	8.01E-15	1.24E+00	3.60E-15	3.57E-15	9.92E-01	5.35E-15	2.42
540	8.44E-15	1.23E+00	3.85E-15	3.82E-15	9.93E-01	5.58E-15	2.48
550	8.87E-15	1.22E+00	4.12E-15	4.09E-15	9.93E-01	5.81E-15	2.55
560	9.32E-15	1.21E+00	4.39E-15	4.36E-15	9.94E-01	6.06E-15	2.62
570	9.78E-15	1.20E+00	4.67E-15	4.65E-15	9.95E-01	6.31E-15	2.68
580	1.03E-14	1.19E+00	4.97E-15	4.95E-15	9.95E-01	6.57E-15	2.74
590	1.07E-14	1.19E+00	5.28E-15	5.26E-15	9.96E-01	6.83E-15	2.81
600	1.12E-14	1.18E+00	5.59E-15	5.57E-15	9.96E-01	7.1E-15	2.87
650	1.40E-14	1.15E+00	7.36E-15	7.35E-15	9.98E-01	8.57E-15	3.18
700	1.70E-14	1.13E+00	9.44E-15	9.43E-15	9.99E-01	1.02E-14	3.48

750	2.05E-14	1.11E+00	1.18E-14	1.18E-14	1.00E+00	1.21E-14	3.77
800	2.44E-14	1.10E+00	1.46E-14	1.46E-14	1.00E+00	1.41E-14	4.05
850	2.87E-14	1.08E+00	1.77E-14	1.77E-14	1.00E+00	1.64E-14	4.32
900	3.35E-14	1.07E+00	2.12E-14	2.12E-14	1.00E+00	1.89E-14	4.58
950	3.87E-14	1.07E+00	2.52E-14	2.52E-14	9.99E-01	2.16E-14	4.84
1000	4.45E-14	1.06E+00	2.95E-14	2.95E-14	9.99E-01	2.46E-14	5.09
1050	5.07E-14	1.05E+00	3.43E-14	3.43E-14	9.98E-01	2.78E-14	5.34
1100	5.75E-14	1.05E+00	3.96E-14	3.95E-14	9.98E-01	3.13E-14	5.59
1150	6.49E-14	1.04E+00	4.54E-14	4.53E-14	9.97E-01	3.51E-14	5.84
1200	7.28E-14	1.04E+00	5.17E-14	5.15E-14	9.97E-01	3.92E-14	6.08
1250	8.14E-14	1.04E+00	5.84E-14	5.82E-14	9.97E-01	4.36E-14	6.32
1300	9.06E-14	1.03E+00	6.58E-14	6.55E-14	9.96E-01	4.83E-14	6.56
1350	1.00E-13	1.03E+00	7.37E-14	7.33E-14	9.96E-01	5.33E-14	6.8
1400	1.11E-13	1.03E+00	8.21E-14	8.17E-14	9.95E-01	5.86E-14	7.03
1450	1.22E-13	1.03E+00	9.12E-14	9.07E-14	9.95E-01	6.43E-14	7.27
1500	1.34E-13	1.03E+00	1.01E-13	1.00E-13	9.94E-01	7.02E-14	7.51
1550	1.46E-13	1.02E+00	1.11E-13	1.10E-13	9.94E-01	7.66E-14	7.74
1600	1.60E-13	1.02E+00	1.22E-13	1.21E-13	9.94E-01	8.33E-14	7.98
1650	1.73E-13	1.02E+00	1.34E-13	1.33E-13	9.93E-01	9.04E-14	8.21
1700	1.88E-13	1.02E+00	1.46E-13	1.45E-13	9.93E-01	9.78E-14	8.45
1750	2.04E-13	1.02E+00	1.59E-13	1.58E-13	9.93E-01	1.06E-13	8.68
1800	2.20E-13	1.02E+00	1.72E-13	1.71E-13	9.92E-01	1.14E-13	8.92
1850	2.37E-13	1.02E+00	1.87E-13	1.85E-13	9.92E-01	1.22E-13	9.15
1900	2.55E-13	1.02E+00	2.02E-13	2.00E-13	9.92E-01	1.31E-13	9.39
1950	2.74E-13	1.02E+00	2.18E-13	2.16E-13	9.91E-01	1.41E-13	9.62
2000	2.93E-13	1.01E+00	2.34E-13	2.32E-13	9.91E-01	1.51E-13	9.86

Table S13. Coordinates (Å) and absolute energies (hartrees) of optimized structures (a) by MN15-L/MG3S

Compound	Absolute energy (hartrees)	Coordinates			
CH ₃ O	-114.973175723	C	0.570372	0.000000	-0.013947
		H	0.879070	-0.000009	1.059965
		H	1.010572	-0.916989	-0.459677
		H	1.010573	0.916996	-0.459663
		O	-0.790306	0.000000	-0.007118
O ₂	-150.236420557	O	0.000000	0.000000	0.602874
		O	0.000000	0.000000	-0.602874
TS1	-265.205979560	O	1.017869	-0.761309	0.000000
		O	1.331958	0.411568	0.000000
		H	0.000000	1.050551	0.000000
		C	-1.175811	0.689733	0.000000
		H	-1.527235	1.180445	0.939395
		H	-1.527235	1.180445	-0.939395
		O	-1.086160	-0.593989	0.000000
HCHO	-114.435477555	C	0.000000	0.000000	-0.526554
		H	0.000000	0.949286	-1.123876
		H	0.000000	-0.949286	-1.123876
		O	0.000000	0.000000	0.675884
HO ₂	-150.816628519	O	0.055519	-0.607113	0.000000
		H	-0.888306	-0.865132	0.000000
		O	0.055519	0.715255	0.000000

(b) by RCCSD(T)-F12a/jun-cc-pVTZ

Compound	Absolute energy (hartrees)	Coordinates		
CH ₃ O	-114.922410	C	-0.5842613485	0.0000000000 -0.0107864830
		H	-0.8731659749	0.0000000000 1.0539149727
		H	-1.0052356725	-0.9057868399 -0.4585008668
		H	-1.0052356725	0.9057868399 -0.4585008668
		O	0.7876156685	0.0000000000 -0.0065667562
O ₂	-150.188486	O	0.0000000000	0.0000000000 -0.6034833921
		O	0.0000000000	0.0000000000 0.6034833921
TS1	-265.104803	O	1.0035099429	-0.7505039117 0.0000000000
		O	1.2892223782	0.4396739002 0.0000000000
		H	0.0357032376	1.0171867778 0.0000000000
		C	-1.1891018510	0.6892283469 0.0000000000
		H	-1.5109904353	1.1766490236 0.9306262225
		H	-1.5109904353	1.1766490236 -0.9306262225
		O	-1.0839668370	-0.5914391603 0.0000000000

(c) by RCCSD(T)-F12a/cc-pVTZ-F12

Compound	Absolute energy (hartrees)	Coordinates			
CH ₃ O	-114.929248	C	-0.5842317392	0.0000000000	-0.0109355280
		H	-0.8730078815	0.0000000000	1.0539920474
		H	-1.0052323814	-0.9059791804	-0.4585254134
		H	-1.0052323814	0.9059791804	-0.4585254134
		O	0.7874213835	0.0000000000	-0.0064456928
O ₂	-150.197846	O	0.0000000000	0.0000000000	-0.6034822169
		O	0.0000000000	0.0000000000	0.6034822169
TS1	-265.120664	O	1.0021262452	-0.7501915875	0.0000000000
		O	1.2882129722	0.4400801665	0.0000000000
		H	0.0375580439	1.0173816866	0.0000000000
		C	-1.1896207252	0.6887700368	0.0000000000
		H	-1.5107884337	1.1762685829	0.9309782271
		H	-1.5107884337	1.1762685829	-0.9309782271
		O	-1.0833136687	-0.5911334683	0.0000000000

CH₃O for MW2-F12 in molpro code

memory,4000,m

Set,Charge=0,Spin=1;

geometry={ANGSTROM;

5

! number of atoms

GeomXYZ

C	-0.5842317392	0.0000000000	-0.0109355280
H	-0.8730078815	0.0000000000	1.0539920474
H	-1.0052323814	-0.9059791804	-0.4585254134
H	-1.0052323814	0.9059791804	-0.4585254134
O	0.7874213835	0.0000000000	-0.0064456928

}

basis=vdz

rks, b3lyp

basis=vdz

rhf

basis=VQZ-F12

rhf

uCCSD-F12b,MAXIT=300,gem_beta=1.4

method(1)='HF(CABS) VQZ-F12';

method(2)='CCSD-F12b VQZ-F12';

e(1)=energr;

e(2)=energy;

basis={

default,cc-pV5Z-F12

set,dfhf

default,av5z/jkfit

set,dfmp

default,awcv5z/mp2fit

}

explicit,df_basis=dfmp,ri_basis=dfmp,df_basis_exch=dfhf,gem_beta=1.4

rhf

UCCSD-F12b

method(3)='HF(CABS) V5Z-F12';

method(4)='CCSD-F12b V5Z-F12';

e(3)=energr;

e(4)=energy;

basis=VQZ

rhf

UCCSD(t),MAXIT=300

method(5)='CCSD VQZ';

method(6)='CCSD(T) VQZ';

e(5)=energc;

e(6)=energy;

basis=V5Z

rhf

uccsd(t),MAXIT=300

method(7)='CCSD V5Z';

method(8)='CCSD(T) V5Z';

e(7)=energc;

e(8)=energy;

Basis=aug-cc-pwCVTZ

rhf

uccsd(t),MAXIT=300

method(9)='CCSD(T) awCVTZ';

e(9)=energy;

```
Basis=aug-cc-pwCVTZ
rhf
{uCCSD(T);
Core;}
method(10)='CCSD(T)(CV)      awCVTZ';
e(10)=energy;
```

```
Basis=aug-cc-pwCVQZ
rhf
uccsd(t),MAXIT=300
method(11)='CCSD(T)      awCVQZ';
e(11)=energy;
```

```
Basis=aug-cc-pwCVQZ
rhf
{uCCSD(T);
Core;}
method(12)='CCSD(T)(CV)      awCVQZ';
e(12)=energy;
```

```
Basis=aug-cc-pVQZ
rhf
uccsd(t),MAXIT=300
method(13)='CCSD(T)      aVQZ';
e(13)=energy;
```

```
Basis=aug-cc-pVQZ-dk
DKroll=1
rhf
uccsd(t),MAXIT=300
method(14)='CCSD(T)CR      aVQZ';
e(14)=energy;
```

```
ehf=e(3);
ecc=(e(4)-e(3))+((e(4)-e(3))-(e(2)-e(1)))/(1.253.2711-1);
e_t=(e(8)-e(7))+((e(8)-e(7))-(e(6)-e(5)))/(1.253.8270-1);
ecv=(e(12)-e(11))+((e(12)-e(11))-(e(10)-e(9)))/(1.33333-1);
ecr=e(14)-e(13)
method(15)='MW2-F12          ';
e(15)=ehf+ecc+e_t+ecv+ecr;
table,method,e;
```

References

- 1 Foster, S. C.; Misra, P.; Lin, T.-Y. D.; Damo, C. P.; Carter, C. C.; Miller, T. A. *J. Phys. Chem.* **1988**, *92*, 5914-5921.
- 2 Chan, B.; Radom, L. W3X: A Cost-Effective Post-CCSD(T) Composite Procedure. *J. Chem. Theory. Comput.* **2013**, *9*, 4769-4778.
- 3 Long, B.; Bao, J. L.; Truhlar, D. G. Unimolecular Reaction of Acetone Oxide and its Reaction with Water in the Atmosphere. *Proc. Natl. Acad. Sci. USA* **2018**, *115*, 6135-6140.
- 4 Sylvetsky, N.; Peterson, K. A.; Karton, A.; Martin, J. M. L. Toward a W4-F12 approach: Can explicitly correlated and orbital-based ab initio CCSD(T) limits be reconciled? *J. Chem. Phys.* **2016**, *144*, 214101.
- 5 Alecu, I. M.; Zheng, J.; Zhao, Y.; Truhlar, D. G. Computational Thermochemistry: Scale Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries. *J. Chem. Theory. Comput.* **2010**, *6*, 2872-2887.
- 6 Marenich, A. V.; Boggs, J. E. A Model Spin-Vibronic Hamiltonian for Twofold Degenerate Electron Systems: A Variational Ab Initio Study of $\tilde{X}^2\text{ECH}_3\text{O}\cdot$. *J. Chem. Phys.* **2004**, *122*, 024308.
- 7 ^{Jaco}_x, M. E. Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules, P.J. Linstrom and W.G. Mallard, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Eds. National Institute of Standards and Technology, Gaithersburg MD, 2018.
- 8 Irikura, K. K. Experimental Vibrational Zero-Point Energies: Diatomic Molecules. *J. Phys. Chem. Ref. Data* **2007**, *36*, 389-397.
- 9 Hu, H.; Dibble, T. S. Quantum Chemistry, Reaction Kinetics, and Tunneling Effects in the Reaction of Methoxy Radicals with O₂. *J. Phys. Chem. A* **2013**, *117*, 14230-14242.
- 10 Peterson, K. A.; Adler, T. B.; Werner, H.-J. Systematically convergent basis sets for explicitly correlated wavefunctions: The atoms H, He, B--Ne, and Al--Ar. *J. Chem. Phys.* **2008**, *128*, 084102.
- 11 Papajak, E.; Truhlar, D. G. Convergent Partially Augmented Basis Sets for Post-Hartree–Fock Calculations of Molecular Properties and Reaction Barrier Heights. *J. Chem. Theory. Comput.* **2011**, *7*, 10-18.
- 12 Papajak, E.; Truhlar, D. G. Efficient Diffuse Basis Sets for Density Functional Theory. *J. Chem. Theory. Comput.* **2010**, *6*, 597-601.
- 13 Frisch, M. J.; Pople, J. A.; Binkley, J. S. Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *J. Chem. Phys.* **1984**, *80*, 3265-3269.
- 14 Lynch, B. J.; Zhao, Y.; Truhlar, D. G. Effectiveness of diffuse basis functions for calculating relative energies by density functional theory. *J. Phys. Chem. A* **2003**, *107*, 1384-1388.
- 15 Dunning, T. H. Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007-1023.
- 16 Chan, B.; Radom, L. W2X and W3X-L: Cost-Effective Approximations to W2 and W4 with kJ mol⁻¹ Accuracy. *J. Chem. Theory. Comput.* **2015**, *11*, 2109-2119.