Supplementary Material

High-accuracy theoretical study on the thermochemistry of several formaldehyde derivatives

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Total energies

It can be seen in Table 1 that beyond the HF level the largest contributions to the total energy can be attributed to the CCSD(T) and relativistic corrections. Generally, the CCSD(T) contribution is larger, however, for the three chlorine-containing molecules, HClCO, FClCO, and Cl₂ the two effects are comparable, and for HClCO and Cl₂ the relativistic correction even exceeds the CCSD(T) contribution. Nevertheless, this is expected because the relativistic effects are more enhanced for second-row than for first-row atoms. As it can be expected, the magnutide of the ZPE and DBOC contributions to the total energy is proportional to the number of bonds and molecular mass, respectively. The profound effect of the perturbative quadruple excitations, $\Delta E_{\text{CCSDT}(Q)}$, is fairly obvious from the data, it exceeds the ΔE_{CCSDT} correction. Consequently, when high accuracy is the goal it seems, that quadruple excitations can not be neglected.

Species	$E_{ m HF}^{\infty}{}^{ m a}$	$\Delta E^{\infty}_{\mathrm{CCSD}(\mathrm{T})}{}^{\mathrm{b}}$	$\Delta E_{\mathrm{CCSDT}}^{\infty}^{\mathrm{c}}$	$\Delta E_{\text{CCSDT}(Q)}^{d}$	$\Delta E_{\rm REL}^{\rm e}$	$\Delta E_{\rm ZPE}^{\rm f}$	$\Delta E_{\rm DBOC}^{\rm g}$	Total
CF ₂ O	-311.770871	-1.282173	0.000468	-0.001916	-0.254691	0.014212	0.009430	-313.285540
FCO	-212.216907	-0.901979	-0.000061	-0.001654	-0.163169	0.008231	0.006802	-213.268737
HFCO	-212.855046	-0.936027	0.000237	-0.001516	-0.163056	0.020799	0.007046	-213.927564
HCICO	-572.881607	-1.269522	-0.000207	-0.001508	-1.516153	0.019033	0.010483	-575.639482
FClCO	-671.795733	-1.618401	0.000098	-0.001912	-1.607806	0.012320	0.012861	-674.998572
cis-HOCO	-188.224981	-0.884980	0.000094	-0.001759	-0.126637	0.020526	0.006757	-189.210982
trans-HOCO	-188.225845	-0.886943	0.000083	-0.001779	-0.126646	0.020850	0.006750	-189.213530
NH ₂ CO	-168.393108	-0.854451	0.000001	-0.001572	-0.102380	0.032845	0.006601	-169.312064
С	-37.693774	-0.151042	-0.000466	-0.000021	-0.016420	0.000000	0.001709	-37.860013
H_2	-1.133661	-0.040912	0.000000	0.000000	-0.000013	0.009930	0.000521	-1.164135
O ₂	-149.691925	-0.635217	0.000112	-0.001908	-0.110911	0.003642	0.004873	-150.431334
F_2	-198.774570	-0.756426	0.000100	-0.001694	-0.183848	0.002093	0.005350	-199.708993
Cl ₂	-919.010527	-1.395247	-0.000841	-0.000708	-2.889747	0.001264	0.012185	-923.283620
N ₂	-108.993257	-0.549274	0.000507	-0.001685	-0.062693	0.005380	0.004125	-109.596897

Table 1: Contributions to the total energies of the species studied in this work. All values are in atomic units.

Table 1 – Continued

- ^a E_{HF}^{∞} was obtained by extrapolating the aug-cc-pCVXZ (X = T, Q, 5) HF-SCF energies.
- ^b $\Delta E_{\text{CCSD}(T)}^{\infty}$ is the all-electron CCSD(T) correlation energy extrapolated to the basis set limit using the aug-cc-pCVXZ (X = Q, 5) basis sets.
- ^c $\Delta E_{\text{CCSDT}}^{\infty}$ is defined by extrapolating the difference $E_{\text{CCSDT}} E_{\text{CCSD}(T)}$ using the cc-pVTZ and cc-pVQZ basis sets in the frozen-core approximation.
- ^d $\Delta E_{\text{CCSDT}(Q)}$ is defined as $E_{\text{CCSDT}(Q)} E_{\text{CCSDT}}$ using the cc-pVDZ basis set.
- ^e ΔE_{REL} was obtained at the CCSD(T)/aug-cc-pCVTZ level of theory. For the carbon atom it includes the spin-orbit correction of -0.000135 E_h .
- ^f Harmonic and anharmonic contributions to the ZPEs along with the G_0 corrections were calculated at the CCSD(T)/ccpVQZ level of theory with all electrons correlated.
- ^g ΔE_{DBOC} was taken from CCSD/aug-cc-pCVTZ calculations.

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Table 2: $\Delta E_{\text{CCSDT}(Q)}$ obtained with cc-pVDZ and cc-pVTZ basis sets. All values are in atomic units.

Species	cc-pVDZ	cc-pVTZ
CF ₂ O	-0.001916	-0.001621
FCO	-0.001654	-0.001543
HFCO	-0.001516	-0.001348
HClCO	-0.001508	-0.001668
cis-HOCO	-0.001759	-0.001681
trans-HOCO	-0.001779	-0.001705
NH ₂ CO	-0.001572	-0.001579
С	-0.000021	-0.000033
O ₂	-0.001908	-0.001826
F_2	-0.001694	-0.001577
Cl ₂	-0.000708	-0.000983
N_2	-0.001685	-0.001793

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
F ₂ CO	R(CF) = 1.30862	((FCO)=126.06	5.925	$\omega_1 = 591$	$x_{11} = 0.0$	-0.9
	R(CO) = 1.17053		11.814	$\omega_2 = 629$	$x_{12} = 0.3$	
			11.885	$\omega_3 = 790$	$x_{13} = 0.0$	
				$\omega_4 = 986$	$x_{14} = -3.5$	
				$\omega_5 = 1286$	$x_{15} = -6.6$	
				$\omega_6 = 1984$	$x_{16} = -1.3$	
					$x_{22} = 0.1$	
					$x_{23} = 0.8$	
					$x_{24} = -0.9$	
					$x_{25} = -4.2$	
					$x_{26} = -6.2$	
					$x_{33} = -0.4$	
					$x_{34} = -2.9$	
					$x_{35} = -6.1$	

Table 3: Calculated bond lengths (in Å), bond angles (in degrees), rotational constants (in GHz), harmonic vibrational frequencies (in cm⁻¹), anharmonicity constants (in cm⁻¹), and G_0 terms (in cm⁻¹) for the species studied in this work.

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
					$x_{36} = -7.2$	
					$x_{44} = -10.0$	
					$x_{45} = -11.2$	
					$x_{46} = 28.2$	
					$x_{55} = -5.3$	
					$x_{56} = -6.0$	
					$x_{66} = -10.7$	
FCO	R(CF) = 1.32289	((FCO)= 127.78	10.888	$\omega_1 = 642$	$x_{11} = -0.7$	2.2
	R(CO) = 1.16728		11.545	$\omega_2 = 1072$	$x_{12} = -11.4$	
			191.389	$\omega_3 = 1922$	$x_{13} = -6.3$	
					$x_{22} = -7.7$	
					$x_{23} = -15.7$	
					$x_{33} = -12.8$	
HFCO	R(CH) = 1.08896	((HCO)= 127.61	10.484	$\omega_1 = 676$	$x_{11} = -0.4$	-4.1
	R(CF) = 1.33682	((FCO)= 122.82	11.829	$\omega_2 = 1040$	$x_{12} = -0.8$	

Table 3 – Continued

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
	R(CO) = 1.17793		92.250	$\omega_3 = 1106$	$x_{13} = -7.6$	
				$\omega_4 = 1386$	$x_{14} = -0.5$	
				$\omega_5 = 1884$	$x_{15} = -5.5$	
				$\omega_6 = 3134$	$x_{16} = 0.4$	
					$x_{22} = -4.3$	
					$x_{23} = -3.6$	
					$x_{24} = 2.4$	
					$x_{25} = -7.8$	
					$x_{26} = -16.4$	
					$x_{33} = -7.1$	
					$x_{34} = -6.9$	
					$x_{35} = -5.6$	
					$x_{36} = 0.3$	
					$x_{44} = -9.1$	
					$x_{45} = 3.9$	

Table 3 – Continued

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
					$x_{46} = -27.9$	
					$x_{55} = -10.7$	
					$x_{56} = -8.8$	
					$x_{66} = -59.9$	
HClCO	R(CH) = 1.09073	((HCO)= 126.29	5.701	$\omega_1 = 465$	$x_{11} = -0.8$	-4.5
	R(CCl) = 1.76609	(ClCO) = 123.51	6.146	$\omega_2 = 756$	$x_{12} = -5.1$	
	R(CO) = 1.18183		78.703	$\omega_3 = 955$	$x_{13} = -1.4$	
				$\omega_4 = 1345$	$x_{14} = -2.3$	
				$\omega_5 = 1824$	$x_{15} = -0.5$	
				$\omega_{6} = 3090$	$x_{16} = 1.4$	
					$x_{22} = -5.4$	
					$x_{23} = -1.8$	
					$x_{24} = -3.4$	
					$x_{25} = 6.3$	
					$x_{26} = -1.3$	

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
					$x_{33} = 1.7$	
					$x_{34} = 6.0$	
					$x_{35} = -8.8$	
					$x_{36} = -12.9$	
					$x_{44} = -10.2$	
					$x_{45} = 13.8$	
					$x_{46} = -29.1$	
					$x_{55} = -11.8$	
					$x_{56} = -15.8$	
					$x_{66} = -63.8$	
FClCO	R(CF) = 1.32082	((FCO)=124.10	3.660	$\omega_1 = 413$	$x_{11} = 0.1$	-0.4
	R(CCl) = 1.72607	((ClCO)= 126.35	5.286	$\omega_2 = 508$	$x_{12} = -0.6$	
	R(CO) = 1.17303		11.895	$\omega_3 = 679$	$x_{13} = -0.1$	
				$\omega_4 = 778$	$x_{14} = -1.7$	
				$\omega_5 = 1134$	$x_{15} = -3.8$	

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
				$\omega_6 = 1920$	$x_{16} = -0.9$	
					$x_{22} = -0.6$	
					$x_{23} = -0.4$	
					$x_{24} = -1.6$	
					$x_{25} = -2.6$	
					$x_{26} = -2.4$	
					$x_{33} = -0.2$	
					$x_{34} = -1.3$	
					$x_{35} = -6.5$	
					$x_{36} = -5.3$	
					$x_{44} = -1.0$	
					$x_{45} = -28.2$	
					$x_{46} = 17.0$	
					$x_{55} = -5.1$	
					$x_{56} = 8.1$	

Table 3 – Continued

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
					$x_{66} = -11.8$	
cis-HOCO	<i>R</i> (C=O)=1.18149	⟨(COH)= 108.10	10.927	$\omega_1 = 582$	$x_{11} = -17.8$	-12.3
	R(C-O) = 1.32642	((OCO)=130.28	11.839	$\omega_2 = 608$	$x_{12} = 1.6$	
	R(OH) = 0.97020		141.998	$\omega_3 = 1089$	$x_{13} = -8.7$	
				$\omega_4 = 1319$	$x_{14} = 17.8$	
				$\omega_5 = 1873$	$x_{15} = -0.9$	
				$\omega_{6} = 3671$	$x_{16} = 1.1$	
					$x_{22} = 0.5$	
					$x_{23} = -6.3$	
					$x_{24} = 0.4$	
					$x_{25} = -8.9$	
					$x_{26} = -4.1$	
					$x_{33} = -7.5$	
					$x_{34} = -18.0$	
					$x_{35} = -12.7$	

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
					$x_{36} = -2.5$	
					$x_{44} = -7.3$	
					$x_{45} = -8.3$	
					$x_{46} = -24.9$	
					$x_{55} = -13.3$	
					$x_{56} = 2.0$	
					$x_{66} = -97.9$	
trans-HOCO	R(C=O)=1.17630	((COH)= 107.83	10.778	$\omega_1 = 539$	$x_{11} = -12.9$	-12.3
	R(C-O) = 1.33928	((OCO)= 127.09	11.518	$\omega_2 = 625$	$x_{12} = 3.2$	
	R(OH) = 0.96068		167.784	$\omega_3 = 1098$	$x_{13} = 8.0$	
				$\omega_4 = 1263$	$x_{14} = -6.4$	
				$\omega_5 = 1913$	$x_{15} = -1.6$	
				$\omega_6 = 3841$	$x_{16} = -9.5$	
					$x_{22} = -0.9$	
					$x_{23} = -8.1$	

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
					$x_{24} = 1.6$	
					$x_{25} = -5.7$	
					$x_{26} = -2.1$	
					$x_{33} = -8.7$	
					$x_{34} = -10.1$	
					$x_{35} = -14.1$	
					$x_{36} = -4.8$	
					$x_{44} = -12.3$	
					$x_{45} = -5.6$	
					$x_{46} = -16.9$	
					$x_{55} = -13.0$	
					$x_{56} = -1.4$	
					$x_{66} = -83.3$	
NH ₂ CO	R(CO) = 1.19092	(NCO)= 129.74	10.335	$\omega_1 = 182$	$x_{11} = 184.3$	73.9
	R(CN) = 1.33941	$\langle (H_s NC) = 120.68$	11.248	$\omega_2 = 537$	$x_{12} = 11.9$	

Table 3 – Continued

Table 3 – Continued

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
	$R(NH_s) = 1.00721$	$\langle (H_a NC)^{\underline{a}} = 119.92$	127.355	$\omega_3 = 623$	$x_{13} = -71.2$	
	$R(NH_a) = 0.99832$			$\omega_4 = 1100$	$x_{14} = 30.8$	
				$\omega_5 = 1242$	$x_{15} = -18.9$	
				$\omega_6 = 1618$	$x_{16} = 14.1$	
				$\omega_7 = 1870$	$x_{17} = 8.9$	
				$\omega_8 = 3559$	$x_{18} = -40.9$	
				$\omega_9 = 3759$	$x_{19} = -65.7$	
					$x_{22} = 0.3$	
					$x_{23} = 0.3$	
					$x_{24} = 9.3$	
					$x_{25} = -5.9$	
					$x_{26} = -8.9$	
					$x_{27} = -2.8$	
					$x_{28} = -3.7$	
					$x_{29} = -2.0$	

constants frequencies constants $x_{33} = 43.9$ $x_{34} = 0.6$ $x_{35} = -197.8$ $x_{36} = 1.3$ $x_{37} = -2.6$ $x_{38} = -0.3$ $x_{39} = -3.2$ $x_{44} = -2.7$ $x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$	Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
$x_{33} = 43.9$ $x_{34} = 0.6$ $x_{35} = -197.8$ $x_{36} = 1.3$ $x_{37} = -2.6$ $x_{38} = -0.3$ $x_{39} = -3.2$ $x_{44} = -2.7$ $x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$				constants	frequencies	constants	
$x_{34} = 0.6$ $x_{35} = -197.8$ $x_{36} = 1.3$ $x_{37} = -2.6$ $x_{38} = -0.3$ $x_{39} = -3.2$ $x_{44} = -2.7$ $x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{33} = 43.9$	
$x_{35} = -197.8$ $x_{36} = 1.3$ $x_{37} = -2.6$ $x_{38} = -0.3$ $x_{39} = -3.2$ $x_{44} = -2.7$ $x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{34} = 0.6$	
$x_{36} = 1.3$ $x_{37} = -2.6$ $x_{38} = -0.3$ $x_{39} = -3.2$ $x_{44} = -2.7$ $x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{35} = -197.8$	
$x_{37} = -2.6$ $x_{38} = -0.3$ $x_{39} = -3.2$ $x_{44} = -2.7$ $x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{36} = 1.3$	
$x_{38} = -0.3$ $x_{39} = -3.2$ $x_{44} = -2.7$ $x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{37} = -2.6$	
$x_{39} = -3.2$ $x_{44} = -2.7$ $x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{38} = -0.3$	
$x_{44} = -2.7$ $x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{39} = -3.2$	
$x_{45} = -5.8$ $x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{44} = -2.7$	
$x_{46} = -18.3$ $x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{45} = -5.8$	
$x_{47} = -7.5$ $x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{46} = -18.3$	
$x_{48} = -3.6$ $x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{47} = -7.5$	
$x_{49} = -9.6$ $x_{55} = -5.9$ $x_{56} = -7.6$						$x_{48} = -3.6$	
$x_{55} = -5.9$ $x_{56} = -7.6$						$x_{49} = -9.6$	
$x_{56} = -7.6$						$x_{55} = -5.9$	
						$x_{56} = -7.6$	

Table 3 – Continued

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
					$x_{57} = -5.6$	
					$x_{58} = -9.9$	
					$x_{59} = -1.2$	
					$x_{66} = -9.0$	
					$x_{67} = -3.0$	
					$x_{68} = -12.9$	
					$x_{69} = -22.2$	
					$x_{77} = -12.6$	
					$x_{78} = 2.4$	
					$x_{79} = -2.1$	
					$x_{88} = -60.3$	
					$x_{89} = -68.3$	
					$x_{99} = -55.5$	
H ₂	R(HH) = 0.74186		1822.287	$\omega_1 = 4403$	$x_{11} = -122.4$	8.3
O ₂	R(OO) = 1.20577		43.465	$\omega_1 = 1604$	$x_{11} = -11.3$	0.3

Table 3 – Continued

Table 3 – Continued

Species	Bond lengths	Bond angles	Rotational	Harmonic vibrational	Anharmonicity	G_0
			constants	frequencies	constants	
F_2	<i>R</i> (FF)=1.41112		26.718	$\omega_1 = 925$	$x_{11} = -11.5$	-0.2
Cl ₂	R(ClCl) = 1.99984		7.227	$\omega_1 = 556$	$x_{11} = -2.6$	0.0
N ₂	R(NN) = 1.09809		59.862	$\omega_1 = 2368$	$x_{11} = -13.9$	0.1

^a H_s and H_a denote the H atom in the *syn* and *anti* position, respectively, relative to the carbonyl oxigen atom.