## 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 $\operatorname{CCSD}(\mathrm{T})$ and relativistic corrections. Generally, the $\operatorname{CCSD}(\mathrm{T})$ contribution is larger, however, for the three chlorine-containing molecules, $\mathrm{HClCO}, \mathrm{FClCO}$, and $\mathrm{Cl}_{2}$ the two effects are comparable, and for HClCO and $\mathrm{Cl}_{2}$ the relativistic correction even exceeds the $\mathrm{CCSD}(\mathrm{T})$ 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, $\Delta E_{\operatorname{CCSDT}(\mathrm{Q})}$, is fairly obvious from the data, it exceeds the $\Delta E_{\text {CCSDT }}$ correction. Consequently, when high accuracy is the goal it seems, that quadruple excitations can not be neglected.

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

| Species | $E_{\mathrm{HF}}^{\infty}$ | $\Delta E_{\mathrm{CCSD}(\mathrm{T})}^{\mathrm{b}}$ | $\Delta E_{\mathrm{CCSDT}}^{\infty}$ | $\Delta E_{\mathrm{CCSDT}(\mathrm{Q})}{ }^{\mathrm{d}}$ | $\Delta E_{\text {REL }} \mathrm{e}$ | $\Delta E_{\text {ZPE }}{ }^{\mathrm{f}}$ | $\Delta E_{\text {DBOC }} \mathrm{g}$ | Total |
| :--- | ---: | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{CF}_{2} \mathrm{O}$ | -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 |
| HClCO | -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 $^{2}$ | -188.225845 | -0.886943 | 0.000083 | -0.001779 | -0.126646 | 0.020850 | 0.006750 | -189.213530 |
| $\mathrm{NH}_{2} \mathrm{CO}$ | -168.393108 | -0.854451 | 0.000001 | -0.001572 | -0.102380 | 0.032845 | 0.006601 | -169.312064 |
| C | -37.693774 | -0.151042 | -0.000466 | -0.000021 | -0.016420 | 0.000000 | 0.001709 | -37.860013 |
| $\mathrm{H}_{2}$ | -1.133661 | -0.040912 | 0.000000 | 0.000000 | -0.000013 | 0.009930 | 0.000521 | -1.164135 |
| $\mathrm{O}_{2}$ | -149.691925 | -0.635217 | 0.000112 | -0.001908 | -0.110911 | 0.003642 | 0.004873 | -150.431334 |
| $\mathrm{~F}_{2}$ | -198.774570 | -0.756426 | 0.000100 | -0.001694 | -0.183848 | 0.002093 | 0.005350 | -199.708993 |
| $\mathrm{Cl}_{2}$ | -919.010527 | -1.395247 | -0.000841 | -0.000708 | -2.889747 | 0.001264 | 0.012185 | -923.283620 |
| $\mathrm{~N}_{2}$ | -108.993257 | -0.549274 | 0.000507 | -0.001685 | -0.062693 | 0.005380 | 0.004125 | -109.596897 |

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## Table 1 - Continued

${ }^{\text {a }} E_{\mathrm{HF}}^{\infty}$ was obtained by extrapolating the aug-cc-pCVXZ $(X=\mathrm{T}, \mathrm{Q}, 5) \mathrm{HF}-\mathrm{SCF}$ energies.
${ }^{\mathrm{b}} \Delta E_{\mathrm{CCSD}(\mathrm{T})}^{\infty}$ is the all-electron $\operatorname{CCSD}(\mathrm{T})$ correlation energy extrapolated to the basis set limit using the aug-cc-pCVXZ ( $X=\mathrm{Q}, 5$ ) basis sets.
${ }^{\mathrm{c}} \Delta E_{\mathrm{CCSDT}}^{\infty}$ is defined by extrapolating the difference $E_{\mathrm{CCSDT}}-E_{\mathrm{CCSD}(\mathrm{T})}$ using the cc-pVTZ and cc-pVQZ basis sets in the frozen-core approximation.
${ }^{\mathrm{d}} \Delta E_{\mathrm{CCSDT}(\mathrm{Q})}$ is defined as $E_{\mathrm{CCSDT}(\mathrm{Q})}-E_{\mathrm{CCSDT}}$ using the cc-pVDZ basis set.
${ }^{\mathrm{e}} \Delta E_{\text {REL }}$ was obtained at the $\operatorname{CCSD}(\mathrm{T}) /$ aug-cc-pCVTZ level of theory. For the carbon atom it includes the spin-orbit correction of $-0.000135 \mathrm{E}_{h}$.
${ }^{\mathrm{f}}$ Harmonic and anharmonic contributions to the ZPEs along with the $G_{0}$ corrections were calculated at the $\operatorname{CCSD}(\mathrm{T}) / \mathrm{cc}-$ pVQZ level of theory with all electrons correlated.
${ }^{\mathrm{g}} \Delta E_{\mathrm{DBOC}}$ was taken from CCSD/aug-cc-pCVTZ calculations.

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

| Species | cc-pVDZ | cc-pVTZ |
| :--- | :---: | :---: |
| $\mathrm{CF}_{2} \mathrm{O}$ | -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 |
| $\mathrm{NH}_{2} \mathrm{CO}$ | -0.001572 | -0.001579 |
| C | -0.000021 | -0.000033 |
| $\mathrm{O}_{2}$ | -0.001908 | -0.001826 |
| $\mathrm{~F}_{2}$ | -0.001694 | -0.001577 |
| $\mathrm{Cl}_{2}$ | -0.000708 | -0.000983 |
| $\mathrm{~N}_{2}$ | -0.001685 | -0.001793 |

Table 3: Calculated bond lengths (in $\AA$ ), bond angles (in degrees), rotational constants (in $\mathbf{G H z}$ ), harmonic vibrational frequencies (in cm ${ }^{-1}$ ), anharmonicity constants (in $\mathrm{cm}^{-1}$ ), and $G_{0}$ terms (in $\mathrm{cm}^{-1}$ ) for the species studied in this work.

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{F}_{2} \mathrm{CO}$ | $R(\mathrm{CF})=1.30862$ | $\langle(\mathrm{FCO})=126.06$ | 5.925 | $\omega_{1}=591$ | $x_{11}=0.0$ | -0.9 |
|  | $R(\mathrm{CO})=1.17053$ |  | 11.814 | $\omega_{2}=629$ | $x_{12}=0.3$ |  |
|  |  |  | 11.885 | $\omega_{3}=790$ | $x_{13}=0.0$ |  |
|  |  |  |  | $\omega_{4}=986$ | $x_{14}=-3.5$ |  |
|  |  |  |  | $\omega_{5}=1286$ | $x_{15}=-6.6$ |  |
|  |  |  |  | $\omega_{6}=1984$ | $x_{16}=-1.3$ |  |
|  |  |  |  |  | $x_{22}=0.1$ |  |
|  |  |  |  |  | $x_{23}=0.8$ |  |
|  |  |  |  |  | $x_{24}=-0.9$ |  |
|  |  |  |  |  | $x_{25}=-4.2$ |  |
|  |  |  |  |  | $x_{26}=-6.2$ |  |
|  |  |  |  |  | $x_{33}=-0.4$ |  |
|  |  |  |  |  | $x_{34}=-2.9$ |  |
|  |  |  |  |  | $x_{35}=-6.1$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $x_{36}=-7.2$ |  |
|  |  |  |  |  | $x_{44}=-10.0$ |  |
|  |  |  |  |  | $x_{45}=-11.2$ |  |
|  |  |  |  |  | $x_{46}=28.2$ |  |
|  |  |  |  |  | $x_{55}=-5.3$ |  |
|  |  |  |  |  | $x_{56}=-6.0$ |  |
|  |  |  |  |  | $x_{66}=-10.7$ |  |
| FCO | $R(\mathrm{CF})=1.32289$ | $\langle(\mathrm{FCO})=127.78$ | 10.888 | $\omega_{1}=642$ | $x_{11}=-0.7$ | 2.2 |
|  | $R(\mathrm{CO})=1.16728$ |  | 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 | $R(\mathrm{CH})=1.08896$ | $\langle(\mathrm{HCO})=127.61$ | 10.484 | $\omega_{1}=676$ | $x_{11}=-0.4$ | -4.1 |
|  | $R(\mathrm{CF})=1.33682$ | $\langle(\mathrm{FCO})=122.82$ | 11.829 | $\omega_{2}=1040$ | $x_{12}=-0.8$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $R(\mathrm{CO})=1.17793$ |  |  | 92.250 | $\omega_{3}=1106$ | $x_{13}=-7.6$ |  |
|  |  |  |  | $\omega_{4}=1386$ | $x_{14}=-0.5$ |  |
|  |  |  |  | $\omega_{5}=1884$ | $x_{15}=-5.5$ |  |
|  |  |  |  | $\omega_{6}=3134$ | $x_{16}=0.4$ |  |
|  |  |  |  |  | $x_{22}=-4.3$ |  |
|  |  |  |  |  | $x_{23}=-3.6$ |  |
|  |  |  |  |  | $x_{24}=2.4$ |  |
|  |  |  |  |  | $x_{25}=-7.8$ |  |
|  |  |  |  |  | $x_{26}=-16.4$ |  |
|  |  |  |  |  | $x_{33}=-7.1$ |  |
|  |  |  |  |  | $x_{34}=-6.9$ |  |
|  |  |  |  |  | $x_{35}=-5.6$ |  |
|  |  |  |  |  | $x_{36}=0.3$ |  |
|  |  |  |  |  | $x_{44}=-9.1$ |  |
|  |  |  |  |  | $x_{45}=3.9$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $x_{46}=-27.9$ |  |
|  |  |  |  |  | $x_{55}=-10.7$ |  |
|  |  |  |  |  | $x_{56}=-8.8$ |  |
|  |  |  |  |  | $x_{66}=-59.9$ |  |
| HClCO | $R(\mathrm{CH})=1.09073$ | $\langle(\mathrm{HCO})=126.29$ | 5.701 | $\omega_{1}=465$ | $x_{11}=-0.8$ | -4.5 |
|  | $R(\mathrm{CCl})=1.76609$ | $\langle(\mathrm{ClCO})=123.51$ | 6.146 | $\omega_{2}=756$ | $x_{12}=-5.1$ |  |
|  | $R(\mathrm{CO})=1.18183$ |  | 78.703 | $\omega_{3}=955$ | $x_{13}=-1.4$ |  |
|  |  |  |  | $\omega_{4}=1345$ | $x_{14}=-2.3$ |  |
|  |  |  |  | $\omega_{5}=1824$ | $x_{15}=-0.5$ |  |
|  |  |  |  | $\omega_{6}=3090$ | $x_{16}=1.4$ |  |
|  |  |  |  |  | $x_{22}=-5.4$ |  |
|  |  |  |  |  | $x_{23}=-1.8$ |  |
|  |  |  |  |  | $x_{24}=-3.4$ |  |
|  |  |  |  |  | $x_{25}=6.3$ |  |
|  |  |  |  |  | $x_{26}=-1.3$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $x_{33}=1.7$ |  |
|  |  |  |  |  | $x_{34}=6.0$ |  |
|  |  |  |  |  | $x_{35}=-8.8$ |  |
|  |  |  |  |  | $x_{36}=-12.9$ |  |
|  |  |  |  |  | $x_{44}=-10.2$ |  |
|  |  |  |  |  | $x_{45}=13.8$ |  |
|  |  |  |  |  | $x_{46}=-29.1$ |  |
|  |  |  |  |  | $x_{55}=-11.8$ |  |
|  |  |  |  |  | $x_{56}=-15.8$ |  |
|  |  |  |  |  | $x_{66}=-63.8$ |  |
| FClCO | $R(\mathrm{CF})=1.32082$ | $\langle(\mathrm{FCO})=124.10$ | 3.660 | $\omega_{1}=413$ | $x_{11}=0.1$ | -0.4 |
|  | $R(\mathrm{CCl})=1.72607$ | $\langle(\mathrm{ClCO})=126.35$ | 5.286 | $\omega_{2}=508$ | $x_{12}=-0.6$ |  |
|  | $R(\mathrm{CO})=1.17303$ |  | 11.895 | $\omega_{3}=679$ | $x_{13}=-0.1$ |  |
|  |  |  |  | $\omega_{4}=778$ | $x_{14}=-1.7$ |  |
|  |  |  |  | $\omega_{5}=1134$ | $x_{15}=-3.8$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | $\omega_{6}=1920$ | $x_{16}=-0.9$ |  |
|  |  |  |  |  | $x_{22}=-0.6$ |  |
|  |  |  |  |  | $x_{23}=-0.4$ |  |
|  |  |  |  |  | $x_{24}=-1.6$ |  |
|  |  |  |  |  | $x_{25}=-2.6$ |  |
|  |  |  |  |  | $x_{26}=-2.4$ |  |
|  |  |  |  |  | $x_{33}=-0.2$ |  |
|  |  |  |  |  | $x_{34}=-1.3$ |  |
|  |  |  |  |  | $x_{35}=-6.5$ |  |
|  |  |  |  |  | $x_{36}=-5.3$ |  |
|  |  |  |  |  | $x_{44}=-1.0$ |  |
|  |  |  |  |  | $x_{45}=-28.2$ |  |
|  |  |  |  |  | $x_{46}=17.0$ |  |
|  |  |  |  |  | $x_{55}=-5.1$ |  |
|  |  |  |  |  | $x_{56}=8.1$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $x_{66}=-11.8$ |  |
| cis-HOCO | $R(\mathrm{C}=\mathrm{O})=1.18149$ | $\langle(\mathrm{COH})=108.10$ | 10.927 | $\omega_{1}=582$ | $x_{11}=-17.8$ | -12.3 |
|  | $R(\mathrm{C}-\mathrm{O})=1.32642$ | $\langle(\mathrm{OCO})=130.28$ | 11.839 | $\omega_{2}=608$ | $x_{12}=1.6$ |  |
|  | $R(\mathrm{OH})=0.97020$ |  | 141.998 | $\omega_{3}=1089$ | $x_{13}=-8.7$ |  |
|  |  |  |  | $\omega_{4}=1319$ | $x_{14}=17.8$ |  |
|  |  |  |  | $\omega_{5}=1873$ | $x_{15}=-0.9$ |  |
|  |  |  |  | $\omega_{6}=3671$ | $x_{16}=1.1$ |  |
|  |  |  |  |  | $x_{22}=0.5$ |  |
|  |  |  |  |  | $x_{23}=-6.3$ |  |
|  |  |  |  |  | $x_{24}=0.4$ |  |
|  |  |  |  |  | $x_{25}=-8.9$ |  |
|  |  |  |  |  | $x_{26}=-4.1$ |  |
|  |  |  |  |  | $x_{33}=-7.5$ |  |
|  |  |  |  |  | $x_{34}=-18.0$ |  |
|  |  |  |  |  | $x_{35}=-12.7$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $x_{36}=-2.5$ |  |
|  |  |  |  |  | $x_{44}=-7.3$ |  |
|  |  |  |  |  | $x_{45}=-8.3$ |  |
|  |  |  |  |  | $x_{46}=-24.9$ |  |
|  |  |  |  |  | $x_{55}=-13.3$ |  |
|  |  |  |  |  | $x_{56}=2.0$ |  |
|  |  |  |  |  | $x_{66}=-97.9$ |  |
| trans-HOCO | $R(\mathrm{C}=\mathrm{O})=1.17630$ | $\langle(\mathrm{COH})=107.83$ | 10.778 | $\omega_{1}=539$ | $x_{11}=-12.9$ | -12.3 |
|  | $R(\mathrm{C}-\mathrm{O})=1.33928$ | $\langle(\mathrm{OCO})=127.09$ | 11.518 | $\omega_{2}=625$ | $x_{12}=3.2$ |  |
|  | $R(\mathrm{OH})=0.96068$ |  | 167.784 | $\omega_{3}=1098$ | $x_{13}=8.0$ |  |
|  |  |  |  | $\omega_{4}=1263$ | $x_{14}=-6.4$ |  |
|  |  |  |  | $\omega_{5}=1913$ | $x_{15}=-1.6$ |  |
|  |  |  |  | $\omega_{6}=3841$ | $x_{16}=-9.5$ |  |
|  |  |  |  |  | $x_{22}=-0.9$ |  |
|  |  |  |  |  | $x_{23}=-8.1$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $x_{24}=1.6$ |  |
|  |  |  |  |  | $x_{25}=-5.7$ |  |
|  |  |  |  |  | $x_{26}=-2.1$ |  |
|  |  |  |  |  | $x_{33}=-8.7$ |  |
|  |  |  |  |  | $x_{34}=-10.1$ |  |
|  |  |  |  |  | $x_{35}=-14.1$ |  |
|  |  |  |  |  | $x_{36}=-4.8$ |  |
|  |  |  |  |  | $x_{44}=-12.3$ |  |
|  |  |  |  |  | $x_{45}=-5.6$ |  |
|  |  |  |  |  | $x_{46}=-16.9$ |  |
|  |  |  |  |  | $x_{55}=-13.0$ |  |
|  |  |  |  |  | $x_{56}=-1.4$ |  |
|  |  |  |  |  | $x_{66}=-83.3$ |  |
| $\mathrm{NH}_{2} \mathrm{CO}$ | $R(\mathrm{CO})=1.19092$ | $\langle(\mathrm{NCO})=129.74$ | 10.335 | $\omega_{1}=182$ | $x_{11}=184.3$ | 73.9 |
|  | $R(\mathrm{CN})=1.33941$ | $\left\langle\left(\mathrm{H}_{s} \mathrm{NC}\right) \underline{\mathrm{a}}=120.68\right.$ | 11.248 | $\omega_{2}=537$ | $x_{12}=11.9$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $R\left(\mathrm{NH}_{s}\right) \underline{\mathrm{a}}=1.00721$ | $\left\langle\left(\mathrm{H}_{a} \mathrm{NC}\right) \stackrel{\text { a }}{ }=119.92\right.$ | 127.355 | $\omega_{3}=623$ | $x_{13}=-71.2$ |  |
|  | $R\left(\mathrm{NH}_{a}\right)=0.99832$ |  |  | $\omega_{4}=1100$ | $x_{14}=30.8$ |  |
|  |  |  |  | $\omega_{5}=1242$ | $x_{15}=-18.9$ |  |
|  |  |  |  | $\omega_{6}=1618$ | $x_{16}=14.1$ |  |
|  |  |  |  | $\omega_{7}=1870$ | $x_{17}=8.9$ |  |
|  |  |  |  | $\omega_{8}=3559$ | $x_{18}=-40.9$ |  |
|  |  |  |  |  | $x_{19}=-65.7$ |  |
|  |  |  |  |  | $x_{22}=0.3$ |  |
|  |  |  |  |  | $x_{23}=0.3$ |  |
|  |  |  |  |  | $x_{24}=9.3$ |  |
|  |  |  |  |  | $x_{25}=-5.9$ |  |
|  |  |  |  |  | $x_{26}=-8.9$ |  |
|  |  |  |  |  | $x_{27}=-2.8$ |  |
|  |  |  |  |  | $x_{28}=-3.7$ |  |
|  |  |  |  |  | $x_{29}=-2.0$ |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational <br> constants |
| :--- | :---: | :---: | :---: |
|  | Harmonic vibrational <br> frequencies | Anharmonicity $G_{0}$ <br> constants |  |
|  | $x_{33}=43.9$ |  |  |
| $x_{34}=0.6$ |  |  |  |
| $x_{35}=-197.8$ |  |  |  |
| $x_{36}=1.3$ |  |  |  |
| $x_{37}=-2.6$ |  |  |  |
| $x_{38}=-0.3$ |  |  |  |
| $x_{39}=-3.2$ |  |  |  |
| $x_{44}=-2.7$ |  |  |  |
| $x_{45}=-5.8$ |  |  |  |
| $x_{46}=-18.3$ |  |  |  |
| $x_{47}=-7.5$ |  |  |  |
|  | $x_{48}=-3.6$ |  |  |
| $x_{49}=-9.6$ |  |  |  |
| $x_{55}=-5.9$ |  |  |  |
| $x_{56}=-7.6$ |  |  |  |

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Table 3 - Continued

| Species | Bond lengths | Bond angles | Rotational constants | Harmonic vibrational frequencies | Anharmonicity constants | $G_{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $x_{57}=-5.6$ |  |
|  |  |  |  |  | $x_{58}=-9.9$ |  |
|  |  |  |  |  | $x_{59}=-1.2$ |  |
|  |  |  |  |  | $x_{66}=-9.0$ |  |
|  |  |  |  |  | $x_{67}=-3.0$ |  |
|  |  |  |  |  | $x_{68}=-12.9$ |  |
|  |  |  |  |  | $x_{69}=-22.2$ |  |
|  |  |  |  |  | $x_{77}=-12.6$ |  |
|  |  |  |  |  | $x_{78}=2.4$ |  |
|  |  |  |  |  | $x_{79}=-2.1$ |  |
|  |  |  |  |  | $x_{88}=-60.3$ |  |
|  |  |  |  |  | $x_{89}=-68.3$ |  |
|  |  |  |  |  | $x_{99}=-55.5$ |  |
| $\mathrm{H}_{2}$ | $R(\mathrm{HH})=0.74186$ |  | 1822.287 | $\omega_{1}=4403$ | $x_{11}=-122.4$ | 8.3 |
| $\mathrm{O}_{2}$ | $R(\mathrm{OO})=1.20577$ |  | 43.465 | $\omega_{1}=1604$ | $x_{11}=-11.3$ | 0.3 |

Continued on Next Page...

Table 3 - Continued

| Species | Bond lengths |  | Bond angles | Rotational | Harmonic vibrational | Anharmonicity |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: |
|  |  | $G_{0}$ |  |  |  |  |
| constants | frequencies | constants |  |  |  |  |
| $\mathrm{F}_{2}$ | $R(\mathrm{FF})=1.41112$ |  | 26.718 | $\omega_{1}=925$ | $x_{11}=-11.5$ | -0.2 |
| $\mathrm{Cl}_{2}$ | $R(\mathrm{ClCl})=1.99984$ |  | 7.227 | $\omega_{1}=556$ | $x_{11}=-2.6$ | 0.0 |
| $\mathrm{~N}_{2}$ | $R(\mathrm{NN})=1.09809$ |  | 59.862 | $\omega_{1}=2368$ | $x_{11}=-13.9$ | 0.1 |

${ }^{\text {a }} \mathrm{H}_{s}$ and $\mathrm{H}_{a}$ denote the H atom in the syn and anti position, respectively, relative to the carbonyl oxigen atom.


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