Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Material: Tert-butyl peroxy radical: ground and first excited state energetics and fundamental frequencies

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1 Treatment of Fermi Resonances

1.1 Expressions

$$X_{ii} = \frac{\phi_{iiii}}{16} - \sum_k \frac{\phi_{iik}^2(8\omega_i^2 - 8\omega_k^2)}{16\omega_k(4\omega_i^2 - \omega_k^2)}$$

$$X_{ij} = \frac{\phi_{iijj}}{4} - \sum_k \frac{\phi_{iik}\phi_{jjk}}{4\omega_k} - \sum_k \phi_{ijk}^2 \frac{\omega_k^2(\omega_i^2 + \omega_j^2 - \omega_k^2)}{16\omega_k(2\Omega_{ijk})} + \sum_\alpha B_\alpha(\xi_{ij}^\alpha)^2\Big(\frac{\omega_i}{\omega_j} + \frac{\omega_j}{\omega_i}\Big)$$

where $\Omega_{ijk} = (\omega_i + \omega_j + \omega_k)(-\omega_i + \omega_j + \omega_k)(\omega_i - \omega_j + \omega_k)(\omega_i + \omega_j - \omega_k)$.

$$G = \sum_r \omega_r n_r + \sum_r X_{rr}(n_r^2 + n_r) + \sum_{s>r} X_{rs}\Big[(n_r n_s + \frac{1}{2}(n_r + n_s))\Big]$$

ν_i^* = deperturbed fundamental frequency of normal mode i
ϕ_{ijk} = cubic force constant having indices i, j, and k
ϕ_{ijkk} = quartic force constant having indices i, j, and k
$D_{r;s} = (3/4)K_{rr;rs} + (3/4)K_{ss;sr} + (1/4)\sum_{t\neq\{r,s\}} K_{rt;st}$
$D_{rt;st} = (3/4)K_{rr;rs} + (3/4)K_{ss;sr} + (3/4)K_{rt;st} + (1/4)\sum_{u\neq\{r,s,t\}} K_{ru;su}$
$D_{rst;rsu} = (1/8)K_{tt;tu} + (1/8)K_{uu;ut} + (1/4)K_{tr;ur} + (1/4)K_{ts;us} + (1/8)\sum_{v\neq\{t,u\}} K_{tv;uv}$
0^{**} denotes elements of the matrices which cannot be computed due to missing 4th-, 5th-, and 6th-derivatives of potential energy

1.2 $\widetilde{\mathrm{X}}\ ^2A''$ State

1.2.1 ν_4, $2\nu_6$, $(\nu_6+\nu_{20}+\nu_{13})$, and $(2\nu_{13}+2\nu_{20})$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_4^* & \frac{1}{4}\phi_{4,6,6} & 0^{**} & 0^{**} \\ \frac{1}{4}\phi_{4,6,6} & 2\nu_6^* & \frac{1}{2}\phi_{6,20,13} & 0^{**} \\ 0^{**} & \frac{1}{2}\phi_{6,20,13} & (\nu_6+\nu_{20}+\nu_{13})^* & \frac{1}{\sqrt{2}}\phi_{6,20,13} \\ 0^{**} & 0^{**} & \frac{1}{\sqrt{2}}\phi_{6,20,13} & (2\nu_{13}+2\nu_{20})^* \end{pmatrix}$$

$$= \begin{pmatrix} 2937.77 & 15.2699 & 0 & 0 \\ 15.2699 & 2964.01 & -2.0433 & 0 \\ 0 & -2.0433 & 2977.67 & -2.8897 \\ 0 & 0 & -2.8897 & 2973.20 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 2979.43, \quad \lambda_2 = 2972.21, \quad \lambda_3 = 2970.27, \quad \lambda_4 = 2930.74$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.01 \\ 0.03 \\ 0.79 \\ 0.17 \end{pmatrix}, \quad L_2 = \begin{pmatrix} 0.03 \\ 0.17 \\ 0.08 \\ 0.71 \end{pmatrix}, \quad L_3 = \begin{pmatrix} 0.14 \\ 0.62 \\ 0.12 \\ 0.12 \end{pmatrix} L_4 = \begin{pmatrix} 0.82 \\ 0.17 \\ 0.00 \\ 0.00 \end{pmatrix}$$

1.2.2 ν_{26}, $(\nu_{28}+\nu_6)$, $(\nu_{27}+\nu_6)$, $(\nu_{28}+\nu_{20}+\nu_{13})$, $(\nu_{27}+\nu_{20}+\nu_{13})$, $(\nu_6+\nu_{18}+\nu_{34})$, and $(\nu_{13}+\nu_{18}+\nu_{20}+\nu_{34})$

Effective Hamiltonian:

$$\begin{pmatrix}
\nu_{26}^{*} & \frac{1}{2\sqrt{2}}\phi_{26,28,6} & \frac{1}{2\sqrt{2}}\phi_{26,27,6} & 0^{**} & 0^{**} & 0^{**} & 0^{**} \\
\frac{1}{2\sqrt{2}}\phi_{26,28,6} & (\nu_{28}+\nu_6)^{*} & D_{rt;st} & \frac{1}{2\sqrt{2}}\phi_{6,20,13} & 0^{**} & \frac{1}{2\sqrt{2}}\phi_{28,18,34} & 0^{**} \\
\frac{1}{2\sqrt{2}}\phi_{26,27,6} & D_{rt;st} & (\nu_{27}+\nu_6)^{*} & 0^{**} & \frac{1}{2\sqrt{2}}\phi_{6,20,13} & \frac{1}{2\sqrt{2}}\phi_{27,18,34} & 0^{**} \\
0^{**} & \frac{1}{2\sqrt{2}}\phi_{6,20,13} & 0^{**} & (\nu_{28}+\nu_{20}+\nu_{13})^{*} & D_{rst;rsu} & 0^{**} & \frac{1}{2\sqrt{2}}\phi_{28,18,34} \\
0^{**} & 0^{**} & \frac{1}{2\sqrt{2}}\phi_{6,20,13} & D_{rst;rsu} & (\nu_{27}+\nu_{20}+\nu_{13})^{*} & 0^{**} & \frac{1}{2\sqrt{2}}\phi_{27,18,34} \\
0^{**} & \frac{1}{2\sqrt{2}}\phi_{28,18,34} & \frac{1}{2\sqrt{2}}\phi_{27,18,34} & 0^{**} & 0^{**} & (\nu_6+\nu_{18}+\nu_{34})^{*} & \frac{1}{2\sqrt{2}}\phi_{6,20,13} \\
0^{**} & 0^{**} & 0^{**} & \frac{1}{2\sqrt{2}}\phi_{28,18,34} & \frac{1}{2\sqrt{2}}\phi_{27,18,34} & \frac{1}{2\sqrt{2}}\phi_{6,20,13} & (\nu_{13}+\nu_{18}+\nu_{20}+\nu_{34})^{*}
\end{pmatrix}$$

$$= \begin{pmatrix}
2928.93 & 19.6201 & 11.3139 & 0 & 0 & 0 & 0 \\
19.6201 & 2926.79 & -0.378435 & -1.44483 & 0 & 5.89828 & 0 \\
11.3139 & -0.378435 & 2954.58 & 0 & -1.44483 & 4.87388 & 0 \\
0 & -1.44483 & 0 & 2942.06 & 0.353430 & 0 & 5.89828 \\
0 & 0 & -1.44483 & 0.353430 & 2968.61 & 0 & 4.87388 \\
0 & 5.89828 & 4.87388 & 0 & 0 & 2940.49 & -1.44483 \\
0 & 0 & 0 & 5.89828 & 4.87388 & -1.44483 & 2950.87
\end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 2970.19, \quad \lambda_2 = 2961.97, \quad \lambda_3 = 2952.75, \quad \lambda_4 = 2943.36$$
$$\lambda_5 = 2939.85, \quad \lambda_6 = 2938.14, \quad \lambda_7 = 2906.06$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.00 \\ 0.00 \\ 0.02 \\ 0.00 \\ 0.90 \\ 0.00 \\ 0.07 \end{pmatrix}, \; L_2 = \begin{pmatrix} 0.19 \\ 0.08 \\ 0.64 \\ 0.00 \\ 0.02 \\ 0.07 \\ 0.00 \end{pmatrix}, \; L_3 = \begin{pmatrix} 0.00 \\ 0.00 \\ 0.01 \\ 0.21 \\ 0.07 \\ 0.01 \\ 0.70 \end{pmatrix} \; L_4 = \begin{pmatrix} 0.18 \\ 0.40 \\ 0.30 \\ 0.00 \\ 0.00 \\ 0.09 \\ 0.02 \end{pmatrix}, \; L_5 = \begin{pmatrix} 0.05 \\ 0.01 \\ 0.00 \\ 0.39 \\ 0.00 \\ 0.48 \\ 0.07 \end{pmatrix}, \; L_6 = \begin{pmatrix} 0.10 \\ 0.03 \\ 0.00 \\ 0.39 \\ 0.00 \\ 0.34 \\ 0.14 \end{pmatrix} \; L_7 = \begin{pmatrix} 0.47 \\ 0.48 \\ 0.03 \\ 0.00 \\ 0.00 \\ 0.02 \\ 0.00 \end{pmatrix}$$

1.2.3 ν_5, $(\nu_8 + \nu_6)$, $(\nu_6 + \nu_{18} + \nu_{15})$, $(\nu_8 + \nu_{20} + \nu_{13})$, and $(\nu_{13} + \nu_{15} + \nu_{18} + \nu_{20})$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_5^* & \frac{1}{2\sqrt{2}}\phi_{5,8,6} & 0^{**} & 0^{**} & 0^{**} \\ \frac{1}{2\sqrt{2}}\phi_{5,8,6} & (\nu_8+\nu_6)^* & \frac{1}{2\sqrt{2}}\phi_{8,15,18} & \frac{1}{2\sqrt{2}}\phi_{6,13,20} & 0^{**} \\ 0^{**} & \frac{1}{2\sqrt{2}}\phi_{8,15,18} & (\nu_{18}+\nu_{15}+\nu_6)^* & 0^{**} & \frac{1}{2\sqrt{2}}\phi_{6,13,20} \\ 0^{**} & \frac{1}{2\sqrt{2}}\phi_{6,13,20} & 0^{**} & (\nu_{20}+\nu_{13}+\nu_8)^* & \frac{1}{2\sqrt{2}}\phi_{8,15,18} \\ 0^{**} & 0^{**} & \frac{1}{2\sqrt{2}}\phi_{6,13,20} & \frac{1}{2\sqrt{2}}\phi_{8,15,18} & (\nu_{13}+\nu_{15}+\nu_{18}+\nu_{20})^* \end{pmatrix}$$

$$= \begin{pmatrix} 2930.14 & 21.8557 & 0 & 0 & 0 \\ 21.8557 & 2930.03 & 3.28025 & -1.44483 & 0 \\ 0 & 3.28025 & 2936.47 & 0 & -1.44483 \\ 0 & -1.44483 & 0 & 2945.80 & 3.28025 \\ 0 & 0 & -1.44483 & 3.28025 & 2946.40 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 2952.55, \quad \lambda_2 = 2949.25, \quad \lambda_3 = 2942.93$$
$$\lambda_4 = 2936.09, \quad \lambda_5 = 2908.01$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.44 \\ 0.46 \\ 0.02 \\ 0.05 \\ 0.02 \end{pmatrix}, \; L_2 = \begin{pmatrix} 0.04 \\ 0.03 \\ 0.00 \\ 0.39 \\ 0.54 \end{pmatrix}, \; L_3 = \begin{pmatrix} 0.00 \\ 0.00 \\ 0.02 \\ 0.56 \\ 0.41 \end{pmatrix}, \; L_4 = \begin{pmatrix} 0.03 \\ 0.00 \\ 0.94 \\ 0.00 \\ 0.02 \end{pmatrix} \; L_5 = \begin{pmatrix} 0.49 \\ 0.50 \\ 0.01 \\ 0.00 \\ 0.00 \end{pmatrix}$$

1.2.4 ν_6 and $(\nu_{20} + \nu_{13})$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_6^* & \frac{1}{2\sqrt{2}}\phi_{6,20,13} \\ \frac{1}{2\sqrt{2}}\phi_{6,20,13} & (\nu_{20}+\nu_{13})^* \end{pmatrix} = \begin{pmatrix} 1482.64 & -1.44483 \\ -1.44483 & 1494.96 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 1495.13, \quad \lambda_2 = 1482.48$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.01 \\ 0.99 \end{pmatrix}, \quad L_2 = \begin{pmatrix} 0.99 \\ 0.01 \end{pmatrix}$$

1.2.5 ν_{28}, ν_{27}, $(\nu_{18} + \nu_{34})$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_{28}^* & D_{28;27} & \frac{1}{2\sqrt{2}}\phi_{28,18,34} \\ D_{28;27} & \nu_{27}^* & \frac{1}{2\sqrt{2}}\phi_{27,18,34} \\ \frac{1}{2\sqrt{2}}\phi_{28,18,34} & \frac{1}{2\sqrt{2}}\phi_{27,18,34} & (\nu_{18}+\nu_{34})^* \end{pmatrix}$$
$$= \begin{pmatrix} 1447.36 & 0.79494 & 5.89828 \\ 0.79494 & 1473.46 & 4.87388 \\ 5.89828 & 4.87388 & 1459.98 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 1475.29, \quad \lambda_2 = 1460.51, \quad \lambda_3 = 1444.99$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.01 \\ 0.88 \\ 0.11 \end{pmatrix}, \quad L_2 = \begin{pmatrix} 0.13 \\ 0.12 \\ 0.75 \end{pmatrix}, \quad L_3 = \begin{pmatrix} 0.86 \\ 0.00 \\ 0.14 \end{pmatrix}$$

1.2.6 ν_8, ν_7, and $(\nu_{18} + \nu_{15})$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_8^* & D_{8;7} & \frac{1}{2\sqrt{2}}\phi_{8,18,15} \\ D_{8;7} & \nu_7^* & \frac{1}{2\sqrt{2}}\phi_{7,18,15} \\ \frac{1}{2\sqrt{2}}\phi_{8,18,15} & \frac{1}{2\sqrt{2}}\phi_{7,18,15} & (\nu_{18}+\nu_{15})^* \end{pmatrix}$$
$$= \begin{pmatrix} 1450.46 & 0.83370 & 3.28025 \\ 0.83370 & 1461.17 & 7.59324 \\ 3.28025 & 7.59324 & 1460.51 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 1469.89, \quad \lambda_2 = 1454.02, \quad \lambda_3 = 1449.23$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.02 \\ 0.49 \\ 0.48 \end{pmatrix}, \quad L_2 = \begin{pmatrix} 0.16 \\ 0.48 \\ 0.37 \end{pmatrix}, \quad L_3 = \begin{pmatrix} 0.82 \\ 0.03 \\ 0.15 \end{pmatrix}$$

1.2.7 ν_{10} and $(\nu_{16} + \nu_{18})$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_{10}^* & \frac{1}{2\sqrt{2}}\phi_{10,18,16} \\ \frac{1}{2\sqrt{2}}\phi_{10,18,16} & (\nu_{18}+\nu_{16})^* \end{pmatrix} = \begin{pmatrix} 1368.17 & -2.0818 \\ -2.0818 & 1361.27 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 1368.75, \quad \lambda_2 = 1360.69$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.93 \\ 0.07 \end{pmatrix}, \quad L_2 = \begin{pmatrix} 0.07 \\ 0.93 \end{pmatrix}$$

1.2.8 ν_{22}, ν_{21}, and $2\nu_{39}$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_{22}^* & D_{22;21} & \frac{1}{4}\phi_{22,39,39} \\ D_{22;21} & \nu_{21}^* & \frac{1}{4}\phi_{21,39,39} \\ \frac{1}{4}\phi_{22,39,39} & \frac{1}{4}\phi_{21,39,39} & 2\nu_{39}^* \end{pmatrix}$$
$$= \begin{pmatrix} 242.490 & -0.922725 & -8.288840 \\ -0.922725 & 269.238 & -14.30530 \\ -8.288840 & -2.0433 & 240.116 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 275.256, \quad \lambda_2 = 247.255, \quad \lambda_3 = 229.332$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.01 \\ 0.84 \\ 0.15 \end{pmatrix}, \quad L_2 = \begin{pmatrix} 0.72 \\ 0.07 \\ 0.21 \end{pmatrix}, \quad L_3 = \begin{pmatrix} 0.27 \\ 0.09 \\ 0.64 \end{pmatrix}$$

1.3 $\widetilde{\mathrm{A}}\ ^2A'$ State

1.3.1 ν_4 and $2\nu_6$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_4^* & \frac{1}{4}\phi_{4,6,6} \\ \frac{1}{4}\phi_{4,6,6} & 2\nu_6^* \end{pmatrix} = \begin{pmatrix} 2937.41 & -15.3434 \\ -15.3434 & 2963.35 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 2970.47, \quad \lambda_2 = 2930.29$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.18 \\ 0.82 \end{pmatrix}, \quad L_2 = \begin{pmatrix} 0.82 \\ 0.18 \end{pmatrix}$$

1.3.2 ν_5 and $(\nu_8 + \nu_6)$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_5^* & \frac{1}{2\sqrt{2}}\phi_{5,8,6} \\ \frac{1}{2\sqrt{2}}\phi_{5,8,6} & (\nu_8+\nu_6)^* \end{pmatrix} = \begin{pmatrix} 2930.82 & 21.9651 \\ 21.9651 & 2931.35 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 2953.05, \quad \lambda_2 = 2909.12$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.49 \\ 0.51 \end{pmatrix}, \quad L_2 = \begin{pmatrix} 0.51 \\ 0.49 \end{pmatrix}$$

1.3.3 ν_{26} and $(\nu_{28} + \nu_6)$

Effective Hamiltonian:

$$\begin{pmatrix} \nu_{26}^* & \frac{1}{2\sqrt{2}}\phi_{26,28,6} \\ \frac{1}{2\sqrt{2}}\phi_{26,28,6} & (\nu_{28}+\nu_6)^* \end{pmatrix} = \begin{pmatrix} 2931.02 & 20.4027 \\ 20.4027 & 2930.30 \end{pmatrix}$$

Eigenvalues:

$$\lambda_1 = 2951.07, \quad \lambda_2 = 2910.26$$

Squared Eigenvectors:

$$L_1 = \begin{pmatrix} 0.51 \\ 0.49 \end{pmatrix}, \quad L_2 = \begin{pmatrix} 0.49 \\ 0.51 \end{pmatrix}$$

2 Scans of ROO$^{\cdot}$

2.1 Optimized coordinates at each approximate value of τ_{CCOO}(see text)

$\tau_{\mathrm{CCOO}} = \mathbf{0}$

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State (a_0):

C	-0.834917986700	0.096829588000	0.000000000000
O	1.538446479900	-1.438953982800	0.000000000000
C	-0.281395217400	2.922031093100	0.000000000000
C	-2.230090682200	-0.733636143800	-2.393196875200
C	-2.230090682200	-0.733636143800	2.393196875200
H	-2.102882927700	3.918236673200	0.000000000000
H	0.786726849600	3.486691654600	-1.681421977000
H	0.786726849600	3.486691654600	1.681421977000
H	-4.100318584800	0.163644125100	-2.468026509800
H	-4.100318584800	0.163644125100	2.468026509800
H	-1.160641070800	-0.184751756600	-4.083952355300
H	-1.160641070800	-0.184751756600	4.083952355300
H	-2.487318128600	-2.792205215800	-2.407925683800
H	-2.487318128600	-2.792205215800	2.407925683800
O	3.655036913600	-0.056849797800	0.000000000000

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.829756263400	0.073656028500	0.000000000000
O	1.468838930000	-1.543208537000	0.000000000000
C	-0.181389714800	2.893971805600	0.000000000000
C	-2.274637159300	-0.661002668000	-2.394863611100
C	-2.274637159300	-0.661002668000	2.394863611100
H	-1.959134079500	3.964818863800	0.000000000000
H	0.899105682200	3.419278239300	-1.689145361200
H	0.899105682200	3.419278239300	1.689145361200
H	-4.092728507600	0.341082913100	-2.466059034100
H	-4.092728507600	0.341082913100	2.466059034100
H	-1.171471694800	-0.169798612500	-4.080715792900
H	-1.171471694800	-0.169798612500	4.080715792900
H	-2.645342278300	-2.701793746000	-2.415941696400
H	-2.645342278300	-2.701793746000	2.415941696400
O	3.709687950200	-0.053221400900	0.000000000000

$\tau_{\mathrm{CCOO}} = \mathbf{5}$

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State (a_0):

C	-0.834820128000	-0.096575219400	0.005433679400
O	1.537545584700	1.439198654700	-0.048919757300
C	-0.284500778400	-2.902858952000	0.338526344000
C	-2.328791849000	0.989794482700	2.229744565600
C	-2.126386958300	0.457184037900	-2.522813650600
H	-2.106373794000	-3.895668559400	0.411584463900
H	0.743444320500	-3.268592353500	2.099002804600
H	0.822044699100	-3.654878695600	-1.240775665600
H	-4.208824176000	0.114193306400	2.311727735900
H	-3.983605377600	-0.467846730300	-2.586029112400
H	-1.343561810900	0.620271264300	4.017518896100
H	-0.975067352300	-0.255154009400	-4.094759834100
H	-2.567394723500	3.039284071200	2.013080404600
H	-2.399192143300	2.498908589800	-2.769502417300
O	3.653971494600	0.057538612700	0.000541568600

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.829448100900	-0.071430341300	0.018793749200
O	1.467164685200	1.505272753900	-0.346714822400
C	-0.183378127800	-2.757804105600	0.879480566900
C	-2.377005647600	1.327761410500	2.019321348400
C	-2.167121599500	-0.104706886200	-2.546432177200
H	-1.960598670000	-3.797785838600	1.138428586200
H	0.838975366200	-2.747187355700	2.682621321600
H	0.953620731200	-3.750911694800	-0.540985735600
H	-4.208705979000	0.385702902800	2.286511824000
H	-3.967542048000	-1.130721067900	-2.401543721500
H	-1.363831742900	1.353857169400	3.828273119600
H	-0.977084261900	-1.038977832100	-3.964941766900
H	-2.723771470500	3.284404131600	1.423947177000
H	-2.559052934900	1.830791777800	-3.180852241100
O	3.708004093300	0.053278346800	-0.011859746600

$\tau_{\mathrm{CCOO}} = \mathbf{10}$

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State (a_0):

C	-0.834537726100	-0.095930323900	0.009882663700
O	1.534863427200	1.440641535600	-0.086378740000
C	-0.293901449000	-2.850951659600	0.649546764900
C	-2.422639003500	1.204911609200	2.044878875800
C	-2.017501488900	0.186143631500	-2.615055279300
H	-2.116848801400	-3.835230523700	0.784617181500
H	0.690290641200	-3.023874831900	2.464476087200
H	0.851015381500	-3.763700588300	-0.812521983300
H	-4.308966473100	0.343059748100	2.124314038800
H	-3.858922962000	-0.770735141800	-2.668654102600
H	-1.523615250100	1.013279130100	3.904490550600
H	-0.787077245700	-0.660047874500	-4.055312557800
H	-2.640366632500	3.223157527700	1.616212936000
H	-2.301866155700	2.188887516800	-3.075419204600
O	3.650815114100	0.059615478600	0.001636337400

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.828539583300	-0.068997650100	0.028020611600
O	1.462274340400	1.466550672500	-0.498565119300
C	-0.189629409700	-2.553025785800	1.368489178200
C	-2.474213564000	1.634225727000	1.682777066200
C	-2.054442530500	-0.580188493800	-2.543812132200
H	-1.965424893600	-3.556908482700	1.750610898100
H	0.773480450900	-2.211523220600	3.171981902600
H	1.001639889700	-3.764337253100	0.180812473100
H	-4.315068004400	0.731722117200	2.014221490100
H	-3.833783906000	-1.623474145900	-2.296815729900
H	-1.553645072600	1.978547561900	3.508356536300
H	-0.781218995600	-1.705170591100	-3.733501386600
H	-2.795011556000	3.456879403200	0.745406551400
H	-2.463898691200	1.205694109300	-3.515838287100
O	3.703086618300	0.055642709300	-0.018174972700

$\tau_{\mathrm{CCOO}} = \mathbf{15}$

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State (a_0):

C	-0.834102765000	-0.095162857800	0.012683520200
O	1.530468050700	1.444655938000	-0.104872716500
C	-0.309843781400	-2.779343529800	0.916001052800
C	-2.511643548300	1.370430363400	1.853592859600
C	-1.903348587700	-0.059107858900	-2.675460719400
H	-2.134292293600	-3.753870505600	1.094288975300
H	0.625016896300	-2.778921311500	2.765665268700
H	0.875016173700	-3.818910518800	-0.423650665200
H	-4.400586461700	0.513459011900	1.918491376100
H	-3.726709072300	-1.050232539300	-2.726709228000
H	-1.700432349700	1.341314045100	3.762524808800
H	-0.597122080900	-1.004423776400	-3.981145881200
H	-2.706827301700	3.343943071200	1.243837032100
H	-2.194157357300	1.891339646800	-3.319571337300
O	3.645692513200	0.063080132400	0.003706664900

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.827075003000	-0.068670436900	0.031297182100
O	1.454565683900	1.461710518000	-0.532445719700
C	-0.200974329200	-2.401524603400	1.625745073100
C	-2.566031430300	1.753985699000	1.443801158000
C	-1.936769112000	-0.851794261700	-2.526124355800
H	-1.974852312800	-3.391836938800	2.050092499300
H	0.702115921600	-1.872105892100	3.414945559100
H	1.041813919700	-3.703815514500	0.597760592800
H	-4.411438626300	0.857918343700	1.765738710100
H	-3.692601709100	-1.927327400500	-2.250685754400
H	-1.740087703200	2.275553613700	3.272430994100
H	-0.584811222400	-2.038408214400	-3.559033721400
H	-2.859242815900	3.478941095700	0.329067827800
H	-2.358713266100	0.823698657500	-3.673393683400
O	3.695337438200	0.061051138300	-0.021404466900

$\tau_{\mathrm{CCOO}} = \mathbf{20}$

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State (a_0):

C	-0.833564369700	-0.094534069900	0.013558634200
O	1.524490004900	1.451991055000	-0.101557170400
C	-0.332705702600	-2.701614070800	1.132992815300
C	-2.595588699400	1.488710958100	1.667427752500
C	-1.784088223500	-0.267860788300	-2.713614009000
H	-2.158577592900	-3.669408946800	1.331807298000
H	0.545026735000	-2.553694615900	3.005291092100
H	0.895220801100	-3.833946768600	-0.086560615800
H	-4.483458672600	0.628158142400	1.706199148800
H	-3.587763286800	-1.294015975000	-2.772847634000
H	-1.873312226100	1.599474025500	3.608778121400
H	-0.406090875800	-1.279992074400	-3.889053464400
H	-2.766911625300	3.412892081500	0.910485250600
H	-2.075060092300	1.626221481200	-3.508252252500
O	3.638825726900	0.067858522000	0.006988205400

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.825117061000	-0.070055031300	0.031548696800
O	1.444697956200	1.477769045800	-0.512337861400
C	-0.218703338900	-2.294754855700	1.781034353200
C	-2.651889629600	1.796778692700	1.262140110200
C	-1.814659717000	-1.024044913200	-2.518168409200
H	-1.990754853300	-3.285818632800	2.211490150800
H	0.623566955600	-1.645295134400	3.560450041800
H	1.072500230200	-3.637202683700	0.871034076500
H	-4.497375484400	0.887919718900	1.543533312600
H	-3.545953581600	-2.140069121900	-2.248787582100
H	-1.921775119500	2.427721024600	3.096932088800
H	-0.389485742400	-2.220655125000	-3.434817459000
H	-2.916049737000	3.454808329400	0.043297545600
H	-2.242329120000	0.573291508300	-3.769925398400
O	3.685419382600	0.068592353900	-0.023239970400

$\tau_{\mathrm{CCOO}} = \mathbf{25}$

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State (a_0):

C	-0.832981580000	-0.094207724600	0.012489607900
O	1.517146760900	1.462177727400	-0.076551603300
C	-0.362935441200	-2.628006467000	1.303097174300
C	-2.673954499000	1.567602508000	1.492938759400
C	-1.660308967300	-0.436924353400	-2.738543911700
H	-2.189311688100	-3.595476023800	1.498297227700
H	0.447492473000	-2.359688919900	3.192903959800
H	0.912569468200	-3.822447927200	0.197558060900
H	-4.557253809100	0.696566374300	1.495778013600
H	-3.443467926400	-1.497056988800	-2.817405054300
H	-2.041038922200	1.793634105900	3.455342363300
H	-0.215566151500	-1.489763385200	-3.791796664800
H	-2.820232980500	3.444351165800	0.620424265700
H	-1.943989831000	1.403825397100	-3.652248481500
O	3.630551753500	0.073744676300	0.011519103200

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.822734233200	-0.072648971900	0.029876218800
O	1.433566300000	1.503165408100	-0.464421992100
C	-0.244419867200	-2.216466981700	1.886941101000
C	-2.730853423700	1.804685050400	1.110774729300
C	-1.689184923400	-1.142804584000	-2.519237164200
H	-2.015353116400	-3.214976251000	2.304909023800
H	0.535730396100	-1.481632901900	3.661619190700
H	1.091973061600	-3.576835526500	1.073879743600
H	-4.572386951300	0.873591717700	1.338224896600
H	-3.396809589600	-2.299977513500	-2.274083495700
H	-2.096655161500	2.509918071600	2.954071789800
H	-0.197701681800	-2.328373046800	-3.339824984400
H	-2.964423586800	3.414965676400	-0.176498229400
H	-2.113682712600	0.397181110600	-3.841859800800
O	3.674225957600	0.077187837200	-0.024108451500

τ_{CCOO} **= 30**

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State (a_0):

C	-0.832410938600	-0.094235309500	0.009586622300
O	1.508769182600	1.473617917600	-0.031264827200
C	-0.400943633700	-2.564954217900	1.431614779400
C	-2.745878076700	1.616308875400	1.333014137000
C	-1.533223162600	-0.567035602800	-2.756882465400
H	-2.225639881400	-3.540648583900	1.598820390600
H	0.329750716900	-2.202165978000	3.338630165500
H	0.927600162200	-3.795069386200	0.433219051700
H	-4.621545267700	0.730179896400	1.292325062800
H	-3.296045881100	-1.657860382200	-2.867232237700
H	-2.201722351200	1.933865401200	3.309299222200
H	-0.028070258700	-1.641685655500	-3.697439220400
H	-2.865887138300	3.451376413300	0.372286951000
H	-1.801052439100	1.228083288400	-3.761668079200
O	3.621335195600	0.080370382700	0.017111520900

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.819991970500	-0.076058619200	0.026718728300
O	1.422229640900	1.530922748100	-0.399916744700
C	-0.279837989700	-2.156869496700	1.965513828700
C	-2.801726531700	1.796084461600	0.975687548900
C	-1.561884310400	-1.228312443000	-2.526270152300
H	-2.050817405600	-3.165433811900	2.358708852800
H	0.435782236500	-1.356728262400	3.739324183900
H	1.098697245100	-3.524349268600	1.239385900500
H	-4.636051962500	0.839140216200	1.144007807200
H	-3.249087170000	-2.421661064200	-2.316727080800
H	-2.262115605200	2.555618991400	2.827471359800
H	-0.012629964100	-2.396322689300	-3.260367185800
H	-3.002923403600	3.370309069800	-0.360725579700
H	-1.971802488700	0.268620523300	-3.901810200100
O	3.662805774800	0.085735191300	-0.024003278100

τ_{CCOO} **= 35**

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State (a_0):

C	-0.831885870100	-0.094572483300	0.005025953000
O	1.499817289000	1.483907051900	0.032282991900
C	-0.446949180200	-2.515766206600	1.524258125200
C	-2.810179025900	1.643660081600	1.188474007400
C	-1.404814671200	-0.660777665300	-2.772746219500
H	-2.266143314800	-3.508847098600	1.639984925200
H	0.190200446500	-2.082411354800	3.450445450200
H	0.940031422500	-3.759359120800	0.627152499800
H	-4.675882099800	0.740490139800	1.098986888200
H	-3.148766062500	-1.776370160200	-2.925816290300
H	-2.352739660900	2.031210129700	3.174221557100
H	0.152802897400	-1.745465176000	-3.610495253100
H	-2.902536812700	3.444577263000	0.162331261200
H	-1.647294558900	1.099089812100	-3.844190470400
O	3.611757762700	0.087220135700	0.023298191900

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.816955784900	-0.079919766800	0.022346645600
O	1.411777852800	1.556672899200	-0.324575397300
C	-0.326555489400	-2.110037346400	2.027313037100
C	-2.863264572300	1.780981559500	0.849063083000
C	-1.434517024200	-1.291232808500	-2.536460464800
H	-2.098802376700	-3.129555604500	2.385246045600
H	0.320271316100	-1.257340076200	3.803246088400
H	1.091627486700	-3.478729183100	1.384721373400
H	-4.688190738400	0.798342859900	0.957964215500
H	-3.107198619300	-2.511364879000	-2.370832926900
H	-2.415301694500	2.583375064800	2.707213552500
H	0.162244706200	-2.444182388200	-3.187540925100
H	-3.029976264500	3.325779679900	-0.525816471300
H	-1.815650193000	0.173246796600	-3.954527225400
O	3.652232452100	0.093189744100	-0.022798061900

τ_{CCOO} **= 40**

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State State (a_0):

C	-0.831386495500	-0.095102198300	-0.000965988000
O	1.490878942000	1.490220962000	0.111383169700
C	-0.500861778600	-2.481159991600	1.586725214700
C	-2.865468538600	1.657722518900	1.058986026100
C	-1.277821213900	-0.722101167700	-2.788130788300
H	-2.309180143300	-3.499341108000	1.630454760600
H	0.029710475600	-1.998611259100	3.533737995900
H	0.948065456300	-3.720821474600	0.786754297100
H	-4.719928888400	0.738315423300	0.917888395400
H	-3.005925683100	-1.853655638300	-2.993540158600
H	-2.490897809500	2.096787590400	3.051368220700
H	0.322533471900	-1.811831257400	-3.533048195100
H	-2.928525443400	3.432238866600	-0.014219415800
H	-1.484799212100	1.013841366800	-3.905171306100
O	3.602476120700	0.093695702600	0.029318803100

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.813710010300	-0.083869809900	0.017050257600
O	1.403153957500	1.577588472700	-0.242227180800
C	-0.385841653500	-2.071525807800	2.078370451400
C	-2.914415780400	1.765849434800	0.725728560200
C	-1.308680519600	-1.338976688100	-2.547096957200
H	-2.159987062600	-3.102825391600	2.390469231600
H	0.185280616300	-1.174493739600	3.858596122400
H	1.070425622000	-3.437411337800	1.520789164200
H	-4.728997987100	0.760195491700	0.778709434000
H	-2.975263041600	-2.572908348200	-2.432178113400
H	-2.553510332900	2.606037184500	2.586183129100
H	0.323626119400	-2.486029814900	-3.114428609100
H	-3.044225648400	3.283615847300	-0.682683053400
H	-1.643884836800	0.100854640000	-4.001529530300
O	3.643438017300	0.098717431700	-0.020333069300

τ_{CCOO} = **45**

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State State (a_0):

C	-0.830815344800	-0.095657423600	-0.008113788100
O	1.482662343700	1.489790305600	0.202324107300
C	-0.562390298800	-2.459498471900	1.625117596500
C	-2.910321302000	1.665818672100	0.943285282400
C	-1.155405591400	-0.756660981300	-2.803373824100
H	-2.354028483100	-3.506572974500	1.582375849400
H	-0.147244232800	-1.945659928400	3.592243058400
H	0.947780081400	-3.684122852500	0.919414811100
H	-4.753615833100	0.733591440700	0.750309004400
H	-2.872416102200	-1.892598312900	-3.067991059100
H	-2.612890206800	2.141776311400	2.940219570600
H	0.476239388900	-1.852747180300	-3.465344335800
H	-2.941919682200	3.420657269300	-0.163051164400
H	-1.316363533900	0.965881467500	-3.948488021400
O	3.594171238000	0.099199001000	0.034254902200

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.810386084400	-0.087570885700	0.011215716800
O	1.396973062600	1.591996075000	-0.156442280500
C	-0.458443873600	-2.036706599000	2.123266826600
C	-2.954490264600	1.755157408800	0.601219991000
C	-1.185469472900	-1.378641279500	-2.555028297300
H	-2.233691430400	-3.081719516400	2.378583707400
H	0.026836067200	-1.099612821600	3.908462315400
H	1.035466878500	-3.395978200500	1.656745881700
H	-4.759081171000	0.730721396700	0.605407281900
H	-2.856148183200	-2.610679353000	-2.496651148500
H	-2.674511232000	2.634213701200	2.457757293800
H	0.468803092200	-2.533958018900	-3.034172273600
H	-3.044773030200	3.243831155000	-0.840712901400
H	-1.454850451600	0.041045495900	-4.042569949000
O	3.637042605200	0.101841480900	-0.016461432400

τ_{CCOO} **= 50**

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State State (a_0):

C	-0.830020114400	-0.096046565700	-0.016052444700
O	1.475986030100	1.480543467600	0.299841979200
C	-0.631506109400	-2.446535443500	1.647150806000
C	-2.943451159500	1.674824936500	0.838422903700
C	-1.040470669500	-0.773063923600	-2.817389221000
H	-2.402427484400	-3.520530519500	1.512480976600
H	-0.333347935800	-1.913683298100	3.630411963900
H	0.933415108700	-3.653250943100	1.033508363500
H	-4.777191312300	0.735394287500	0.595997800700
H	-2.752819690300	-1.899651694500	-3.144068322300
H	-2.715948207200	2.178397768400	2.837809731800
H	0.609588344800	-1.882623759400	-3.405285505900
H	-2.940452384600	3.414286235500	-0.292253511300
H	-1.144532306600	0.943655029800	-3.977839898700
O	3.587533719400	0.103188864500	0.037334950500

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.807179501700	-0.090765762400	0.005372551100
O	1.393387283900	1.599347326700	-0.072060164800
C	-0.544379619600	-1.998798411400	2.167453328300
C	-2.983217299400	1.751801257000	0.470028278000
C	-1.065346080700	-1.419439915200	-2.555596874400
H	-2.317658094200	-3.061235188300	2.356257887300
H	-0.158188582200	-1.020621910700	3.954884530600
H	0.987572457300	-3.346974157900	1.803476216600
H	-4.779391676800	0.713526322200	0.436805229400
H	-2.750582802200	-2.632548653000	-2.558056686500
H	-2.776707893100	2.678152175800	2.313299851400
H	0.595847556900	-2.600198528100	-2.937763374200
H	-3.031269992800	3.203434008800	-1.010888878800
H	-1.247142157800	-0.020803111700	-4.076002711000
O	3.633216809200	0.102527097100	-0.011172928100

τ_{CCOO} = **55**

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State State (a_0):

C	-0.828889053800	-0.096174370000	-0.023990238500
O	1.471691976200	1.463084127000	0.392775392000
C	-0.708919431000	-2.430514150700	1.670015272700
C	-2.963862418900	1.693266786400	0.733963919300
C	-0.934867421300	-0.791938655500	-2.825545594600
H	-2.458930868000	-3.524621338500	1.451155444300
H	-0.521487720000	-1.876593666600	3.660973571500
H	0.898901248700	-3.626793247100	1.150634240700
H	-4.791115765800	0.752793510800	0.450216937300
H	-2.650266852200	-1.895578235800	-3.209061480500
H	-2.798377736100	2.228518724300	2.731269160800
H	0.719667932200	-1.928661825600	-3.341930358900
H	-2.921621897900	3.414189401400	-0.423833959600
H	-0.970349446100	0.917824069500	-4.000406742400
O	3.583244589000	0.105326216400	0.037964192200

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.804330748700	-0.093350577100	0.000374611100
O	1.392065714300	1.600514866700	0.000477791300
C	-0.642764595300	-1.942700294400	2.222556832500
C	-3.000677657000	1.757285635400	0.320836731000
C	-0.948324065100	-1.479306041200	-2.538551019700
H	-2.408393323200	-3.027790071200	2.342353545100
H	-0.370290443700	-0.910908801400	4.000792791500
H	0.927240365700	-3.274699158200	1.981799077700
H	-4.791085172300	0.710104203300	0.268599522600
H	-2.656469189400	-2.657968054700	-2.600490524100
H	-2.859339108000	2.751876747100	2.134660680700
H	0.703907954500	-2.702796520900	-2.806866899000
H	-3.003601328700	3.152724610600	-1.213588636200
H	-1.021325192600	-0.114512188600	-4.098311834300
O	3.631633917100	0.101173089300	-0.004955689500

τ_{CCOO} **= 60**

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{X}}$ State State (a_0):

C	-0.827097686500	-0.101436474600	0.000000000000
O	1.470585983000	1.515377721000	0.000000000000
C	-0.817870609000	-1.709064153700	2.398288594800
C	-2.970696097600	1.833514640700	0.000000000000
C	-0.817870609000	-1.709064153700	-2.398288594800
H	-2.548083077000	-2.852875117700	2.472549029200
H	-0.750722938000	-0.500559132900	4.083546966100
H	0.821920584000	-2.974985636600	2.412268415000
H	-4.795671941900	0.846941776900	0.000000000000
H	-2.548083077000	-2.852875117700	-2.472549029200
H	-2.871117841700	3.037535503300	1.686381688000
H	0.821920584000	-2.974985636600	-2.412268415000
H	-2.871117841700	3.037535503300	-1.686381688000
H	-0.750722938000	-0.500559132900	-4.083546966100
O	3.581977491600	0.110908164900	0.000000000000

Cartesian Coordinates of Optimized Geometry of $\widetilde{\mathrm{A}}$ State (a_0):

C	-0.801390412900	-0.096201398300	0.000000000000
O	1.392824303300	1.598425786300	0.000000000000
C	-0.793993069600	-1.715243562800	2.400480334100
C	-3.006660659400	1.773299802500	0.000000000000
C	-0.793993069600	-1.715243562800	-2.400480334100
H	-2.537855606600	-2.838340500600	2.486670454800
H	-0.694243704000	-0.504913588400	4.081494882700
H	0.822462757200	-3.013154070900	2.422648028100
H	-4.794992542100	0.721399267900	0.000000000000
H	-2.537855606600	-2.838340500600	-2.486670454800
H	-2.941425674600	2.976624863000	1.687638191300
H	0.822462757200	-3.013154070900	-2.422648028100
H	-2.941425674600	2.976624863000	-1.687638191300
H	-0.694243704000	-0.504913588400	-4.081494882700
O	3.631949562500	0.097493290500	0.000000000000

3 Optimized Geometries of ROO·

3.1 $\widetilde{\mathrm{X}}\ ^2A''$ Geometries

Cartesian Coordinates for the $\widetilde{\mathrm{X}}\ ^2A''$ equilibrium structure optimized at the UHF-CCSD(T)/ANO1 level (Å):

O	-0.7794064054	0.7881950817	0.0000000000
O	-1.8829820733	0.0607889719	0.0000000000
C	0.4384567260	-0.0541381241	0.0000000000
C	1.5581751840	0.9739974320	0.0000000000
H	2.5231182980	0.4637641570	0.0000000000
H	1.4989810941	1.6067285354	-0.8872460506
H	1.4989810941	1.6067285354	0.8872460506
C	0.4339511151	-0.9003231634	-1.2632886696
H	-0.4279312053	-1.5674664729	-1.2681906607
H	0.3952335018	-0.2640088526	-2.1493982009
H	1.3454173649	-1.5004416921	-1.3036969354
C	0.4339511151	-0.9003231634	1.2632886696
H	-0.4279312053	-1.5674664729	1.2681906607
H	0.3952335018	-0.2640088526	2.1493982009
H	1.3454173649	-1.5004416921	1.3036969354

Cartesian Coordinates for the $\widetilde{\mathrm{X}}\ ^2A''$ equilibrium structure optimized at the UHF-CCSD(T)/ANO0 level (Å):

O	-0.7782006433	0.8019034131	0.0000000000
O	-1.8955009888	0.0586900856	0.0000000000
C	0.4376812750	-0.0536778827	0.0000000000
C	1.5720248004	0.9702542332	0.0000000000
H	2.5377605055	0.4481822736	0.0000000000
H	1.5193302613	1.6073946638	-0.8923948023
H	1.5193302613	1.6073946638	0.8923948023
C	0.4327985141	-0.9043978653	-1.2691197637
H	-0.4349417138	-1.5742947115	-1.2765175716
H	0.3972654896	-0.2648844875	-2.1609201359
H	1.3483875575	-1.5096766289	-1.3084167149
C	0.4327985141	-0.9043978653	1.2691197637
H	-0.4349417138	-1.5742947115	1.2765175716
H	0.3972654896	-0.2648844875	2.1609201359
H	1.3483875575	-1.5096766289	1.3084167149

Cartesian Coordinates for the $\widetilde{\mathrm{X}}\ ^2A''$ equilibrium structure optimized at the ROHF-CCSD(T)/ANO0 level (Å):

O	-0.7780184899	0.8020204406	0.0000000000
O	-1.8955948490	0.0587018545	0.0000000000
C	0.4375925266	-0.0536394274	0.0000000000
C	1.5720977634	0.9701353588	0.0000000000
H	2.5377598811	0.4479234001	0.0000000000
H	1.5194934543	1.6072839440	-0.8923951357
H	1.5194934543	1.6072839440	0.8923951357
C	0.4327504014	-0.9044150635	-1.2691071057
H	-0.4350909259	-1.5741983801	-1.2765710450
H	0.3973633239	-0.2649137351	-2.1609246868
H	1.3482422665	-1.5098420762	-1.3083332530
C	0.4327504014	-0.9044150635	1.2691071057
H	-0.4350909259	-1.5741983801	1.2765710450
H	0.3973633239	-0.2649137351	2.1609246868
H	1.3482422665	-1.5098420762	1.3083332530

3.2 $\widetilde{\mathrm{A}}\ ^2A'$ Geometries

Cartesian Coordinates for the $\widetilde{\mathrm{A}}\ ^2A'$ equilibrium structure optimized at the UHF-CCSD(T)/ANO1 level (Å):

O	-0.7435128048	0.8294791041	0.0000000000
O	-1.9035081074	0.0525659384	0.0000000000
C	0.4251364562	-0.0517626527	0.0000000000
C	1.5744345572	0.9447100695	0.0000000000
H	2.5217579050	0.4021144095	0.0000000000
H	1.5316703361	1.5770196992	-0.8879486762
H	1.5316703361	1.5770196992	0.8879486762
C	0.4221988293	-0.9029078503	-1.2648599027
H	-0.4254182643	-1.5892092971	-1.2738590751
H	0.3637649660	-0.2646297151	-2.1476823913
H	1.3428515697	-1.4889022096	-1.3133465407
C	0.4221988293	-0.9029078503	1.2648599027
H	-0.4254182643	-1.5892092971	1.2738590751
H	0.3637649660	-0.2646297151	2.1476823913
H	1.3428515697	-1.4889022096	1.3133465407

Cartesian Coordinates for the $\widetilde{\mathrm{A}}\ ^2A'$ equilibrium structure optimized at the UHF-CCSD(T)/ANO0 level (Å):

O	-0.7370509261	0.8458505623	0.0000000000
O	-1.9219450978	0.0515912786	0.0000000000
C	0.4240775831	-0.0509075869	0.0000000000
C	1.5910564855	0.9383898939	0.0000000000
H	2.5374010036	0.3817479753	0.0000000000
H	1.5565357082	1.5751620701	-0.8930597717
H	1.5565357082	1.5751620701	0.8930597717
C	0.4201630368	-0.9076678790	-1.2702795508
H	-0.4352289776	-1.5944921318	-1.2820104315
H	0.3673785375	-0.2671887845	-2.1598342536
H	1.3429750955	-1.5019857361	-1.3158891210
C	0.4201630368	-0.9076678790	1.2702795508
H	-0.4352289776	-1.5944921318	1.2820104315
H	0.3673785375	-0.2671887845	2.1598342536
H	1.3429750955	-1.5019857361	1.3158891210

Cartesian Coordinates for $\widetilde{\mathrm{A}}\ ^2A'$ equilibrium structure optimized at ROHF-CCSD(T)/ANO0 level (Å):

O	-0.7362702256	0.8465933684	0.0000000000
O	-1.9228425242	0.0516822548	0.0000000000
C	0.4241931925	-0.0509691249	0.0000000000
C	1.5917786431	0.9376827544	0.0000000000
H	2.5377852075	0.3804620534	0.0000000000
H	1.5576597178	1.5744726579	-0.8930650159
H	1.5576597178	1.5744726579	0.8930650159
C	0.4198296710	-0.9077148171	-1.2702844987
H	-0.4359862250	-1.5940163168	-1.2820242853
H	0.3674215914	-0.2672030988	-2.1598385611
H	1.3422812701	-1.5025961156	-1.3159023663
C	0.4198296710	-0.9077148171	1.2702844987
H	-0.4359862250	-1.5940163168	1.2820242853
H	0.3674215914	-0.2672030988	2.1598385611
H	1.3422812701	-1.5025961156	1.3159023663

4 Focal Point Analysis

Table 1: Extrapolation schemes for the Hartree-Fock energies.

Method	Formula	X Points*	Ref.
exp	$E(X) = E_{\rm HF}^{\infty} + Ae^{-BX}$	{3,4,5}	[A]
expGauss	$E(X) = E_{\rm HF}^{\infty} + Ae^{-(X-1)} + Be^{-(X-1)^2}$	{3,4,5}	[B]
exp-2	$E(X) = E_{\rm HF}^{\infty} + Ae(X+1)e^{-\sqrt{X}}$	{3,4,5}	[C]
SchwenkeHF	$E_{\rm HF}^{\infty} = [E(X_2) - E(X_1)]F_{X_2} + E(X_1)$	{4,5}	[D]

Table 2: Extrapolation Schemes for the correlation energies.

Method	Formula	X Points*	Ref.
X^{-3}	$\epsilon(X) = \epsilon^{\infty} + AX^{-3}$	{3,4,5}	[E]
Schwartz4	$\epsilon(X) = \epsilon^{\infty} + A(X+\frac{1}{2})^{-4}$	{3,4,5}	[F]
Schwartz6	$\epsilon(X) = \epsilon^{\infty} + A(X+\frac{1}{2})^{-4} + B(X+\frac{1}{2})^{-4}$	{3,4,5}	[F]
SchwenkeCCSD**	$\epsilon^{\infty} = [\epsilon(X_2) - \epsilon(X_1)]F_{X_2} + \epsilon(X_1)$	{4,5}	[D]
SchwenkeCCSD(T)**	$\epsilon^{\infty} = [\epsilon(X_2) - \epsilon(X_1)]F_{X_2} + \epsilon(X_1)$	{4,5}	[D]

References:
[A] Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.
[B] Peterson, K. A.; Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *100*, 7410.
[C] Karton, A.; Martin, J. M. L. *Theor. Chem. Acc.* **2006**, *115*, 330.
[D] Schwenke, D. W. *J. Chem. Phys.* **2005**, *122*, 014107.
[E] Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.
[F] Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669.

* X = 3, 4, and 5 denote the usage of the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, respectively
** Not used in this study; the CCSD and CCSD(T) correlation energies were obtained with additivity

Table 3: Summary of computed energies (see below for FPA tables).

Scheme	$\epsilon_{\rm HF}$	$\epsilon_{\rm MP2}$	$\epsilon_{\rm CCSD}$	$\epsilon_{\rm CCSD(T)}$	$T_{e,\rm CBS}[\rm cm^{-1}]$
1	exp	$X(-3)$	add	add	7817
2	expGauss	$X(-3)$	add	add	7820
3*	exp-2	$X(-3)$	add	add	7820
4	exp	Schwartz6	add	add	7813
5	expGauss	Schwartz6	add	add	7816
6	exp-2	Schwartz6	add	add	7816
7	exp	Schwartz4	add	add	7813
8	expGauss	Schwartz4	add	add	7816
9	exp-2	Schwartz4	add	add	7817
10	SchwenkeHF	$X(-3)$	add	add	7820
				Mean	7817
				Std. Dev.	2

* Published in the main article

Table 4: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 1.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4755]	[+2643]	[+86]	[+334]	[7817]
Extrap. Fx'n	exp	$X(-3)$	add	add	fp limit
Extrap. Points	3,4,5	4,5			

Table 5: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 2.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4758]	[+2643]	[+86]	[+334]	[7820]
Extrap. Fx'n	expGauss	$X(-3)$	add	add	fp limit
Extrap. Points	3,4,5	4,5			

Table 6: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 3.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4758]	[+2643]	[+86]	[+334]	[7820]
Extrap. Fx'n	exp-2	$X(-3)$	add	add	fp limit
Extrap. Points	4,5	4,5			

Table 7: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 4.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4755]	[+2639]	[+86]	[+334]	[7813]
Extrap. Fx'n	exp	Schwartz6	add	add	fp limit
Extrap. Points	3,4,5	3,4,5			

Table 8: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 5.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4758]	[+2639]	[+86]	[+334]	[7816]
Extrap. Fx'n	expGauss	Schwartz6	add	add	fp limit
Extrap. Points	3,4,5	3,4,5			

Table 9: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 6.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4758]	[+2639]	[+86]	[+334]	[7816]
Extrap. Fx'n	exp-2	Schwartz6	add	add	fp limit
Extrap. Points	4,5	3,4,5			

Table 10: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 7.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4758]	[+2643]	[+86]	[+334]	[7820]
Extrap. Fx'n	SchwenkeHF	$X(-3)$	add	add	fp limit
Extrap. Points	4,5	4,5			

Table 11: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 8.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4755]	[+2639]	[+86]	[+334]	[7813]
Extrap. Fx'n	exp	Schwartz4	add	add	fp limit
Extrap. Points	3,4,5	4,5			

Table 12: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 9.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4758]	[+2639]	[+86]	[+334]	[7816]
Extrap. Fx'n	expGauss	Schwartz4	add	add	fp limit
Extrap. Points	3,4,5	4,5			

Table 13: Incremented Focal Point Table for $T_{e,\mathrm{CBS}}$, as computed via Extrapolation Scheme 10.

	ROHF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	4685	+2529	+87	+201	7503
cc-pVTZ	4732	+2570	+71	+311	7684
cc-pVQZ	4758	+2614	+86	+334	7792
cc-pV5Z	4758	+2628	[+86]	[+334]	[7805]
CBS LIMIT	[4758]	[+2639]	[+86]	[+334]	[7817]
Extrap. Fx'n	exp-2	Schwartz4	add	add	fp limit
Extrap. Points	4,5	4,5			

5 Vibrational Frequencies of ROO·

5.1 $\widetilde{\mathrm{X}}\ ^2A''$ State

5.1.1 Harmonic Vibrational Frequencies

	UHF				ROHF	
	ANO1		ANO0		ANO0	
ν	ω	Int.	ω	Int.	ω	Int.
ν_1	3144.6704	14.9130	3161.1824	14.1380	3161.0782	14.2139
ν_2	3132.1091	29.5223	3148.8214	29.0730	3148.8033	29.1184
ν_3	3125.2019	3.5707	3142.1005	3.7142	3142.0914	3.6857
ν_4	3049.2341	8.0377	3058.0804	7.6368	3058.0549	7.6058
ν_5	3044.1790	8.5015	3052.2552	10.8356	3052.2372	10.8521
ν_6	1523.3927	10.6715	1526.9757	9.3960	1526.9824	9.4001
ν_7	1499.9394	3.7019	1503.7349	2.4673	1503.7341	3.1816
ν_8	1489.2634	0.1576	1493.0890	0.0100	1493.0927	0.1241
ν_9	1422.6930	6.2494	1425.9094	5.6360	1425.8963	5.6499
ν_{10}	1401.8739	23.4444	1404.6674	19.7913	1404.6552	19.7642
ν_{11}	1308.3588	11.9207	1305.6455	13.9904	1305.6143	13.9588
ν_{12}	1221.0428	26.3648	1217.0352	33.2392	1217.1098	33.3478
ν_{13}	1167.3855	18.0835	1101.9164	17.0945	1097.6054	16.8325
ν_{14}	1056.2918	0.2820	1054.2993	0.4330	1054.0961	0.5001
ν_{15}	938.3066	0.5918	935.9877	0.2768	935.9545	0.2668
ν_{16}	852.7791	6.7763	851.3983	7.8311	851.6685	7.8291
ν_{17}	751.0075	1.8362	742.1450	2.1814	742.2613	2.1672
ν_{18}	549.2456	6.3041	543.5184	5.9725	543.5596	5.9130
ν_{19}	399.3943	0.4979	399.9052	0.4477	399.9121	0.4460
ν_{20}	360.6613	2.4265	360.3185	2.0950	360.3052	2.0852
ν_{21}	272.9744	1.8038	271.1578	1.6892	271.1333	1.6816
ν_{22}	253.6777	0.0532	255.9962	0.0460	255.9630	0.0458
ν_{23}	3141.3028	3.4384	3157.9058	2.7637	3157.8015	2.7812
ν_{24}	3131.0417	19.5355	3146.7977	19.1551	3146.7843	19.1591
ν_{25}	3123.2811	3.8128	3140.3177	2.8793	3140.3147	2.8738
ν_{26}	3044.5387	14.4153	3053.2664	16.6914	3053.2352	16.7000
ν_{27}	1499.4367	3.2592	1503.7321	3.1853	1503.7352	2.4637
ν_{28}	1489.8248	0.0061	1493.8664	0.1249	1493.8660	0.0097
ν_{29}	1471.2498	0.0005	1476.4153	0.0104	1476.4186	0.0105
ν_{30}	1398.2294	18.9606	1401.2121	16.1985	1401.1994	16.2082
ν_{31}	1279.6372	12.2233	1277.9914	15.7721	1277.9650	15.7866
ν_{32}	1045.0519	0.4167	1044.0167	0.4813	1044.0208	0.4825
ν_{33}	964.8305	0.0047	963.4465	0.0091	963.4184	0.0090
ν_{34}	936.4116	0.1907	934.9073	0.0842	934.8740	0.0833
ν_{35}	438.3359	3.1430	437.9182	3.1348	437.9954	3.1378
ν_{36}	333.2805	1.0734	332.8828	1.1730	332.9046	1.1734
ν_{37}	247.8984	0.0333	252.3709	0.0233	252.3762	0.0233
ν_{38}	190.6659	0.0439	197.0810	0.0268	197.0982	0.0268
ν_{39}	126.6355	0.2289	126.0623	0.1224	126.1355	0.1192

5.2 $\widetilde{\mathrm{A}}\ ^2A'$ State

5.2.1 Harmonic Vibrational Frequencies

	UHF				ROHF	
	ANO1		ANO0		ANO0	
ν	ω	Int.	ω	Int.	ω	Int.
ν_1	3137.5664	21.7762	3153.0940	21.1309	3153.0640	21.1378
ν_2	3133.2130	28.4191	3149.9548	27.8049	3149.9218	27.7922
ν_3	3125.9047	6.9888	3142.8116	7.3006	3142.7847	7.3220
ν_4	3049.3522	7.2855	3057.7438	6.9418	3057.7173	6.9469
ν_5	3044.7239	10.0694	3052.8091	12.6230	3052.7840	12.6314
ν_6	1521.0461	7.4600	1524.6768	6.6282	1524.6652	6.6357
ν_7	1498.5710	5.1403	1502.7756	4.4253	1502.7591	4.4383
ν_8	1488.4302	0.0093	1492.2853	0.0305	1492.2751	0.0302
ν_9	1424.1516	8.8985	1427.9374	8.2437	1427.9189	8.2213
ν_{10}	1401.3424	18.0270	1403.8376	14.3079	1403.7879	14.2978
ν_{11}	1297.0770	9.5454	1294.3594	11.2661	1294.2354	11.2614
ν_{12}	1215.3053	59.2136	1218.4410	60.5778	1218.4357	60.5679
ν_{13}	1050.6259	0.3629	1050.0590	0.3343	1049.9445	0.3346
ν_{14}	968.9891	33.5795	912.0641	35.4822	894.2200	46.8100
ν_{15}	933.7065	4.2057	940.3790	6.0634	938.1621	2.0983
ν_{16}	863.9629	24.1200	860.4596	12.1737	852.0514	4.8908
ν_{17}	739.6618	6.8729	732.7052	5.6868	731.6016	5.2062
ν_{18}	495.3253	4.7703	495.4414	3.5221	494.8086	3.3965
ν_{19}	403.3702	0.5781	403.5986	0.5394	403.3573	0.5180
ν_{20}	347.0822	1.7443	347.1481	1.3249	346.9416	1.3068
ν_{21}	254.4933	0.9591	251.0867	1.1853	250.8425	1.1925
ν_{22}	250.3726	0.6780	255.4757	0.0805	255.4643	0.0732
ν_{23}	3137.3377	24.1002	3152.6253	22.5144	3152.6013	22.5302
ν_{24}	3133.3449	0.0012	3148.9789	0.1567	3148.9530	0.1538
ν_{25}	3123.3952	2.4937	3140.3423	2.0873	3140.3128	2.0793
ν_{26}	3043.0233	11.0787	3051.4933	13.3097	3051.4670	13.3095
ν_{27}	1498.1805	2.3871	1502.6475	1.6935	1502.6396	1.6954
ν_{28}	1486.6907	0.1064	1490.8442	0.2003	1490.8347	0.2004
ν_{29}	1470.2101	0.1014	1475.9293	0.0982	1475.9277	0.0981
ν_{30}	1402.5774	20.2834	1405.8197	16.5688	1405.8170	16.5616
ν_{31}	1283.2407	15.9390	1281.1296	19.8270	1281.1122	19.8162
ν_{32}	1049.7074	0.9061	1049.1292	0.9721	1049.1311	0.9705
ν_{33}	964.2981	0.0045	963.1637	0.0014	963.1476	0.0014
ν_{34}	927.2604	0.0245	926.0975	0.0000	926.1070	0.0000
ν_{35}	457.4991	4.1390	455.8021	3.7545	455.7932	3.7514
ν_{36}	337.7717	0.9660	336.7865	1.0013	336.7607	1.0006
ν_{37}	254.8351	0.0019	258.5267	0.0000	258.5031	0.0000
ν_{38}	197.0948	0.0138	202.2361	0.0176	202.1925	0.0176
ν_{39}	112.1590	0.1410	111.3291	0.2223	111.2185	0.2232