Supporting Information

The Highest Oxidation State of Rhodium: Rhodium(VII) in \([\text{RhO}_3]^+\)

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1 Experimental details

$[\text{RhO}_n]^+ \ (n = 0 − 3)$ molecular ions were produced by argon sputtering of a rhodium target in the presence of oxygen, which was introduced as a mixture of 1% oxygen in helium carrier gas. In the plasma region of the ion source, ozone is formed that reacts to produce cationic, anionic and neutral rhodium-oxygen species of different sizes and compositions.\cite{1,2-4} The magnetron sputter source was kept at room temperature.

The cationic species are directed via electrostatic fields and a radio frequency ion guide to a radio frequency quadrupole mass filter, where the ions of interest are selected. The mass selected ions are guided into a linear radio frequency quadrupole ion trap, which is cooled by liquid helium. The ion trap has a pulsed exit aperture where the stored ions are extracted in bunches, and are thereafter mass analyzed by a reflectron time-of-flight mass spectrometer. Fig. S1 shows the mass spectra of the investigated species, $[\text{RhO}_n]^+$ ($n = 0 − 3$).

The ion trap is aligned with the beamline, allowing the interaction of the X-rays with the stored ions. X-ray absorption by the ions is followed by multiple Auger decay leading to the dissociation of the ions due to Coulomb repulsion. The ion yield spectrum is obtained by monitoring the product ion intensity with the time-of-flight mass spectrometer, while scanning the photon energy over an absorption edge. The incident photon energy was scanned in steps of 160 meV with a photon energy bandwidth of 345 meV at the oxygen K-edge and steps of 150 meV with a photon energy bandwidth of 300 meV at the rhodium M3-edge.

The oxygen K-edge spectra obtained from different ion yield channels are shown in Fig. S2. The most intense product ions, Rh$^{2+}$ and O$^+$ for samples $[\text{RhO}_{1.2}]^+$, and Rh$^+$ and O$^+$ for $[\text{RhO}_{3.4}]^+$, resulted in very similar ion yield spectra for a respective parent ion, indicating that the partial ion yield spectra are a good approximation of the total ion yield, and thus to the X-ray absorption spectrum. The figure in the main text uses the ion yield channel that showed the highest signal-to-noise ratio, which is the O$^+$ yield in all cases.

For the rhodium M3-edge plots, only the Rh$^{2+}$ product ion was observed with significant intensity, therefore, all plots shown are from the Rh$^{2+}$ yield channel. All ion yield spectra showed in this work are normalized to a 0–1 intensity range.
Figure S1: TOF mass spectra of trapped, mass-selected ions $[\text{RhO}_n]^+$ ($n = 0 - 3$).

Figure S2: Oxygen K-edge spectra from different ion yield channels of the $[\text{RhO}_n]^+$ ($n = 1 - 4$) series.
2 Rhodium M$_3$-edge spectra

Fig. S3 shows the rhodium M$_3$-edge spectra of the cationic rhodium-oxo series [RhO$_n$]$^+$ ($n = 0 – 3$), indicating the chemical shift on the position of the peak median along the series as the oxidation state (OS) of the rhodium atom increases.

In order to minimize the experimental uncertainty, only the energy range that comprises the absorption peak was considered to calculate the median (Table S1). We plot the integral value for this region, done with the raw data, as a function of the energy. We then extract the energy position of the point at half of the height of the integral curve. This process was done individually for two scans of each sample and the average value of the median was considered.

Table S1: Energy range considered to calculate the median of Rh M$_3$-edge.

|          | Energy range (eV)       |
|----------|-------------------------|
| Rh$^+$   | 488.00 – 501.56 ± 0.15   |
| [RhO]$^+$| 488.00 – 501.56 ± 0.15   |
| [RhO$_2$]$^+$ | 490.04 – 503.48 ± 0.15 |
| [RhO$_3$]$^+$ | 489.95 – 504.95 ± 0.15 |

Figure S3: Ion yield spectra at the rhodium M$_3$-edge of the rhodium oxides series [RhO$_n$]$^+$ ($n = 0 – 3$). The Rh$^{2+}$ yield channel is shown here for all spectra. The black dashed lines indicate the position of the peak median.
3 The case of [RhO₄]⁺

In this study, also the [RhO₄]⁺ species was observed, although at much lower intensity, as evidenced by the smaller signal-to-noise ratio when comparing the mass spectrum of the selected [RhO₄]⁺ (Fig. S4) with the other rhodium-oxo species in Fig. S1. The presence of a σ*-like transition around 540 eV at the oxygen K-edge of [RhO₄]⁺ in Fig. 3 suggests the presence of an O₂ unit. The rhodium M₃-edge spectrum is shown in Fig. S5. The peak median at the rhodium M₃-edge was calculated subtracting a linear background from the raw data and extracting the half of the peak integral. The position of the Rh M₃-edge median of [RhO₄]⁺ is at 497.90 ± 0.15 eV, which when inserted in the equation of the linear fit showed in Fig. 3, predicts an OS = 4.6 ± 0.3 for the Rh atom in [RhO₄]⁺. Therefore, two possibilities arise, a cationic peroxo-superoxo system for OS(Rh) = 4, or a cationic diperoxo system for an OS(Rh) = 5, and a distinction could be made by a deeper theoretical study combined with these results. Though it is not clear how the oxygen atoms are bonded to the Rh atom in the [RhO₄]⁺ system, it is evident that we do not have a cationic tetroxide system and the trioxide cation is the highest-oxidized rhodium-oxo system we could produce.

Figure S4: Mass spectrum of selected ions [RhO₄]⁺.

Figure S5: Ion yield spectrum of [RhO₄]⁺ at the rhodium M₃-edge, where the dashed black line indicates the position of the peak median. The Rh²⁺ yield channel is shown here.
4 Computational results

The structures were optimized using spin-restricted (closed-shell species) and spin-unrestricted (open-shell species) density functional theory (DFT) methods, B3LYP \[10,11\] and M06-L,\[10,11\] combined with the triple zeta def2-TZVP basis sets and the associated ECP.\[12,14\] using TURBOMOLE 7.1,\[15\] as well as at the CCSD(T)/aug-cc-pVTZ(-PP) level using Molpro 2019.\[18-20\] The stability of the spin-restricted DFT ground state was verified by the positivity of the lowest eigenvalues in all IRREPs for B3LYP and M06L. The X-ray absorption spectrum was calculated using time-dependent density functional theory (TD-DFT) BP86\[8,21\] together with the ZORA-def2-TZVP(O)/SARC-ZORA-TZVP(Rh) level. The pre-edge region of the oxygen K-edge X-ray absorption spectrum of the \[\sigma^s\] state was calculated using TD-DFT following the procedure outlined by Ray\[26\] at the BP86/ZORA-def2-TZVP(O)/SARC-ZORA-TZVP(Rh) level. The lowest excited state, \(0^1\) with an occupation pattern of \(\sigma^s\) \(\sigma^v\) \(\sigma^e\) \(\sigma^v\), is prone to Jahn-Teller distortion and geometry relaxation leads to two triplet states of lower symmetries, \(2^1\) and \(3^1\). Their corresponding electronic configurations are \((\sigma^s)^2(\sigma^v)^1(\sigma^e)^1\) and \((\sigma^s)^2(\sigma^v)^1(\sigma^e)^1\), respectively. The lowest \(5^1\) quintet state \((1^1)\) with an electron population of \((\sigma^s)^2(\sigma^v)^1(\sigma^e)^1(\sigma^v)^1\) shows a highly symmetric \(D_{3h}\) point group symmetry. Lastly, the stationary point of \(3^1\), the third triplet state \((2^1)\) with an occupation pattern of \((\sigma^s)^2(\sigma^v)^1(\sigma^e)^1(\sigma^v)^1\) exhibits \(C_{2v}\) symmetry, despite its totally symmetric charge distribution at the high symmetric reference geometry (Table S9). Vibrational analyses of the stationary points obtained at the DFT level were performed, see Tables S6-S10 that also lists the point groups in which the electronic structure calculations were performed.

The pre-edge region of the oxygen K-edge X-ray absorption spectrum of the \(S_0, T_1\) and \(T_2\) states shown in Fig. S6 was calculated using TD-DFT following the procedure outlined by Ray\[26\] at the BP86/ZORA-def2-TZVP(O)/SARC-ZORA-TZVP(Rh) level. Due to the degenerate nature of the oxygen 1s orbitals in \(D_{3h}\) point group symmetry 25 excitations from only one of the localized molecular orbitals corresponding to the oxygen
1s atomic orbitals into the entire virtual space were considered.

Figure S6: TD-DFT calculated X-ray absorption spectra at the oxygen K-edge for the $S_0$, $T_1$ and $T_2$ states of $[\text{RhO}_3]^+$. The relative energies shown in Table S2 were calculated by using the lowest single point energy for the respective method at the given stationary point (Tables S3–S5). The singlet-triplet energy gap was predicted to be 17–75 kJ mol$^{-1}$. The almost identical energies gaps for both active spaces suggest that perturbative treatment of the CASSCF(14,20) recovers most of the correlation energy neglected by excluding the Rh(4s) orbital.

The CASPT2 method is suspected to systematically underestimate energies of open-shell states. [27, 28] A recent study has shown that this effect is minimal for organic chromophores using small basis sets, but often a stronger effect is still assumed for transition metal complexes in combination with larger basis sets. [29] Hence, the CCSD(T) and NEVPT2 energies of 46–64 kJ mol$^{-1}$ can be considered a more reliable estimation of the singlet-triplet gap.
Table S2: Energy levels of the lowest electronic states. The enthalpy differences ($\Delta H$, $T = 0$ K) were calculated from the electronic energies and the zero point energies.

| State | $\Delta H_{\text{CCSD(T)}}$ | $\Delta H_{\text{CASSCF}(14)}^a$ | $\Delta H_{\text{CASSCF}(15)}^a$ | $\Delta H_{\text{NEVPT2}(14)}^a$ | $\Delta H_{\text{CASPT2}(14)}^a$ | $\Delta H_{\text{CASPT2}(15)}^a$ |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $S_0$ | 0               | 0               | 0               | 0               | 0               | 0               |
| $T_1$ | 67              | 61              | 75              | 46              | 18              | 17              |
| $T_2$ | 64              | 60              | 75              | 47              | 22              | 21              |
| $Q_1$ | 147             | 140             | 136             | 136             | 113             | 113             |
| $T_3$ | 217             | 180             | 213             | 190             | 163             | 169             |

$^a$ The number indicates the number of active orbitals in the CASSCF reference function.

Table S3: Single point energies at the optimized structures obtained at the B3LYP level. Electronic energies, $E$, in Hartree. The relative enthalpy at $T = 0$ K with respect to the lowest energy ($H = E + \text{ZPE}_{\text{B3LYP}}$) in kJ mol$^{-1}$.

|          | $S_0$          | $T_1$          | $T_2$          | $Q_1$          | $T_3$          |
|----------|----------------|----------------|----------------|----------------|----------------|
| $E_{\text{B3LYP}}$ ($\Delta H$) | -335.658222 (15) | -335.662280 (0) | -335.653436 (1) | -335.643283 (49) | -335.596945 (174) |
| $E_{\text{CCSD(T)}}$ ($\Delta H$) | -334.614266 (0) | -334.588170 (65) | -334.589457 (64) | -334.557437 (145) | -334.531778 (215) |
| $E_{\text{CASSCF}(14,20)}$ ($\Delta H$) | -5004.958955 (0) | -5004.936747 (54) | -5004.937825 (55) | -5004.906417 (133) | -5004.891432 (176) |
| $E_{\text{NEVPT2}(14,20)}$ ($\Delta H$) | -5005.789557 (0) | -5005.772890 (40) | -5005.773159 (42) | -5005.738227 (130) | -5005.718805 (184) |
| $E_{\text{CASPT2}(14,20)}$ ($\Delta H$) | -5005.849851 (0) | -5005.846074 (6) | -5005.84855 (12) | -5005.809427 (102) | -5005.790823 (153) |
| $E_{\text{CASSCF}(15,20)}$ ($\Delta H$) | -5004.995830 (0) | -5004.968538 (68) | -5004.969039 (70) | -5004.938918 (145) | -5004.916064 (208) |
| $E_{\text{CASPT2}(15,20)}$ ($\Delta H$) | -5005.848412 (0) | -5005.843908 (8) | -5005.806632 (102) | -5005.786036 (162) |

$^a$ CASPT2(15,20) omitted due to high computational cost in $C_s$ point group symmetry.
Table S4: Single point energies at the optimized structures obtained at the M06L level. Electronic energies, $E$, in Hartree. The relative enthalpy at $T = 0$ K with respect to the lowest energy ($H = E + ZPE_{M06L}$) in kJ mol$^{-1}$.

|        | $S_0$        | $T_1$          | $T_2$          | $Q_1$          | $T_3$          |
|--------|--------------|----------------|----------------|----------------|----------------|
| $E_{M06L}$ ($\Delta H$) | -335.850841 (0) | -335.847309 (7) | -335.842265 (22) | -335.816094 (71) | -335.781630 (181) |
| $E_{CCSD(T)}$ ($\Delta H$) | -334.615159 (0) | -334.588210 (68) | -334.589693 (66) | -334.557450 (147) | -334.531888 (218) |
| $E_{CASSCF(14,20)}$ ($\Delta H$) | -5004.960110 (0) | -5004.936767 (59) | -5004.938137 (57) | -5004.906580 (136) | -5004.892106 (178) |
| $E_{NEVPT2(14,20)}$ ($\Delta H$) | -5005.790690 (0) | -5005.773110 (43) | -5005.773396 (45) | -5005.738233 (134) | -5005.719038 (187) |
| $E_{CASPT2(14,20)}$ ($\Delta H$) | -5005.851585 (0) | -5005.846099 (12) | -5005.844963 (17) | -5005.809533 (106) | -5005.791306 (158) |
| $E_{CASSCF(15,20)}$ ($\Delta H$) | -5004.997061 (0) | -5004.968473 (72) | -5004.969379 (72) | -5004.939128 (148) | -5004.916765 (210) |
| $E_{CASPT2(15,20)}$ ($\Delta H$) | -5005.849752 (0) | -5005.843943 (12) | -5005.846099 (12) | -5005.806732 (109) | -5005.786496 (169) |

* CASPT2(15,20) omitted due to high computational cost in $C_s$ point group symmetry.

Table S5: Single point energies at the optimized structures obtained at the CCSD(T) level. Electronic energies, $E$, in Hartree. The relative enthalpy at $T = 0$ K with respect to the lowest energy ($H = E + ZPE_{CCSD(T)}$) in kJ mol$^{-1}$.

|        | $S_0$        | $T_1$          | $T_2$          | $Q_1$          | $T_3$          |
|--------|--------------|----------------|----------------|----------------|----------------|
| $E_{CCSD(T)}$ ($\Delta H$) | -334.616036 (0) | -334.588876 (67) | -334.592308 (62) | -334.557450 (149) | -334.531908 (219) |
| $E_{CASSCF(14,20)}$ ($\Delta H$) | -5004.961634 (0) | -5004.934790 (67) | -5004.938418 (60) | -5004.906593 (140) | -5004.892467 (180) |
| $E_{NEVPT2(14,20)}$ ($\Delta H$) | -5005.792044 (0) | -5005.771274 (51) | -5005.774069 (47) | -5005.738232 (137) | -5005.719131 (190) |
| $E_{CASPT2(14,20)}$ ($\Delta H$) | -5005.851385 (0) | -5005.844560 (22) | -5005.847567 (22) | -5005.809541 (113) | -5005.791551 (163) |
| $E_{CASSCF(15,20)}$ ($\Delta H$) | -5004.998787 (0) | -5004.968473 (80) | -5004.969379 (72) | -5004.939128 (148) | -5004.916765 (210) |
| $E_{CASPT2(15,20)}$ ($\Delta H$) | -5005.851785 (0) | -5005.843943 (12) | -5005.846099 (12) | -5005.806740 (114) | -5005.786496 (169) |

* Converged to $C_{2v}$ point group symmetry.
Table S6. Optimized structures, point groups used for calculations and vibrational data for the \(S_0\) electronic state.

| Energy | Rh   | O1 | O2 | O3 |
|--------|------|----|----|----|
| B3LYP/def2-TZVP (\(D_{3h} \cdot ^1A_1\')) |
| Energy = -335.6582219614 | -0.0000000 | 0.0000000 | 0.0000000 |
| 0 | 0.8339636 | -1.4444674 | 0.0000000 |
| 0 | 0.8339636 | 1.4444674 | 0.0000000 |
| 0 | -1.6679273 | 0.0000000 | 0.0000000 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|----------------|
| 7 | a2'' | 113.24 | 6.71473 | YES | NO |
| 8 | e' | 282.86 | 0.54286 | YES | YES |
| 9 | e' | 282.86 | 0.54286 | YES | YES |
| 10 | e' | 931.71 | 34.56424 | YES | YES |
| 11 | e' | 931.71 | 34.56424 | YES | YES |
| 12 | a1' | 957.71 | 0.00000 | NO | YES |

M06L/def2-TZVP (\(D_{3h} \cdot ^1A_1\'))

| Energy | Rh   | O1 | O2 | O3 |
|--------|------|----|----|----|
| Energy = -335.8508407745 | -0.0000000 | 0.0000000 | 0.0000000 |
| 0 | 0.8378061 | -1.4511227 | 0.0000000 |
| 0 | 0.8378061 | 1.4511227 | 0.0000000 |
| 0 | -1.6756121 | 0.0000000 | 0.0000000 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|----------------|
| 7 | a2'' | 45.64 | 5.32851 | YES | NO |
| 8 | e' | 278.61 | 0.35281 | YES | YES |
| 9 | e' | 278.61 | 0.35281 | YES | YES |
| 10 | e' | 915.01 | 34.98778 | YES | YES |
| 11 | e' | 915.01 | 34.98778 | YES | YES |
| 12 | a1' | 926.68 | 0.00000 | NO | YES |

RHF/UCCSD(T)/aug-cc-pVTZ (\(C_2v \cdot ^1A_1\))

| Energy | Rh   | O1 | O2 | O3 |
|--------|------|----|----|----|
| UCCSD(T)/AUG-CC-PVTZ,RH=AUG-CC-PVTZ-PP Energy=-334.61603634 | -0.0000000 | 0.0000000 | 0.0000000 |
| 0 | 0.0000000 | -1.467516638 | 0.847271126 |
| 0 | 0.0000000 | 1.467516638 | 0.847271126 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|----------------|
| 7 | b1 | 175.66 | 15.49053 | YES | YES |
| 8 | b2 | 214.70 | 1.08030 | YES | YES |
| 9 | a1 | 263.95 | 0.64144 | YES | YES |
| 10 | b2 | 682.80 | 6.69940 | YES | YES |
| 11 | a1 | 739.50 | 11.23338 | YES | YES |
| 12 | a1 | 768.80 | 4.58906 | YES | YES |

Table S7. Optimized structures, point groups used for calculations and vibrational data for the \(T_1\) electronic state.

| Energy | Rh   | O1 | O2 | O3 |
|--------|------|----|----|----|
| B3LYP/def2-TZVP (\(C_2 \cdot ^3A_2\)) |
| Energy = -335.662206982 | -0.0000000 | 0.0000000 | -0.0509802 |
| 0 | 0.0000000 | 1.4369856 | 0.9084276 |
| 0 | 0.0000000 | -1.4369856 | 0.9084276 |
| 0 | -1.7658750 | 0.0000000 | 0.0000000 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|----------------|
| 7 | b1 | 175.66 | 15.49053 | YES | YES |
| 8 | b2 | 214.70 | 1.08030 | YES | YES |
| 9 | a1 | 263.95 | 0.64144 | YES | YES |
| 10 | b2 | 682.80 | 6.69940 | YES | YES |
| 11 | a1 | 739.50 | 11.23338 | YES | YES |
| 12 | a1 | 768.80 | 4.58906 | YES | YES |

M06L/def2-TZVP (\(C_2 \cdot ^3A_2\))

| Energy | Rh   | O1 | O2 | O3 |
|--------|------|----|----|----|
| Energy = -335.8473093563 | -0.0000000 | 0.0000000 | -0.0604150 |
| 0 | 0.0000000 | 1.4203087 | 0.9160031 |
| 0 | 0.0000000 | -1.4203087 | 0.9160031 |
| 0 | -1.7715912 | 0.0000000 | 0.0000000 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|----------------|
| 7 | b1 | 168.27 | 16.01832 | YES | YES |
| 8 | b2 | 197.96 | 1.13187 | YES | YES |
\begin{table}[h]
\centering
\begin{tabular}{cccccc}
  \hline
  \textbf{No.} & \textbf{Symbol} & \textbf{Energy} & \textbf{Freq.} & \textbf{IR Intensity} & \textbf{Sel. Rules} \\
  \hline
  9 & a1 & 277.40 & 0.24854 & YES & YES \\
  10 & b2 & 710.82 & 10.36639 & YES & YES \\
  11 & a1 & 745.84 & 6.75616 & YES & YES \\
  12 & a1 & 804.68 & 15.66957 & YES & YES \\
  \hline
\end{tabular}
\caption{Optimized structures, point groups used for calculations and vibrational data for the $T_2$ electronic state.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{cccccc}
  \hline
  \textbf{No.} & \textbf{Symbol} & \textbf{Energy} & \textbf{Freq.} & \textbf{IR Intensity} & \textbf{Sel. Rules} \\
  \hline
  7 & a' & 220.36 & 8.12959 & YES & YES \\
  8 & a' & 270.79 & 1.50722 & YES & YES \\
  9 & a' & 313.96 & 0.16221 & YES & YES \\
  10 & a' & 686.16 & 1.03030 & YES & YES \\
  11 & a' & 862.75 & 1.95507 & YES & YES \\
  12 & a'' & 1033.38 & 24.5569 & YES & YES \\
  \hline
\end{tabular}
\caption{Vibrational data for the $T_2$ electronic state.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{cccccc}
  \hline
  \textbf{No.} & \textbf{Symbol} & \textbf{Energy} & \textbf{Freq.} & \textbf{IR Intensity} & \textbf{Sel. Rules} \\
  \hline
  7 & b' & 268.57 & 9.29295 & YES & YES \\
  8 & a' & 271.57 & 1.11387 & YES & YES \\
  9 & a' & 301.11 & 8.91067 & YES & YES \\
  10 & a' & 714.42 & 0.96350 & YES & YES \\
  11 & a' & 876.28 & 1.95507 & YES & YES \\
  12 & a'' & 904.82 & 0.39949 & YES & YES \\
  \hline
\end{tabular}
\caption{Vibrational data for the $T_2$ electronic state.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{cccccc}
  \hline
  \textbf{No.} & \textbf{Symbol} & \textbf{Energy} & \textbf{Freq.} & \textbf{IR Intensity} & \textbf{Sel. Rules} \\
  \hline
  7 & b' & 268.57 & 0.04553 & YES & YES \\
  8 & a' & 268.68 & 12.52429 & YES & YES \\
  9 & b' & 304.02 & 12.52429 & YES & YES \\
  10 & a' & 773.35 & 7.92149 & YES & YES \\
  11 & b2 & 773.38 & 7.92149 & YES & YES \\
  12 & a' & 853.26 & 0.00000 & YES & YES \\
  \hline
\end{tabular}
\caption{Vibrational data for the $T_3$ electronic state.}
\end{table}
| Cartesian coordinates | 4 | Energy = -335.7816295267 |
|-----------------------|---|--------------------------|
| Rh                    | 0.0000000 | 0.0000000 | 0.0001973 |
| 0                     | 0.0000000 | 1.4833074 | 0.8560654 |
| 0                     | 0.0000000 | -1.4833074 | 0.8560654 |
| 0                     | 0.0000000 | 0.0000000 | -1.7123281 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|-----------------|
| 7 | a1   |          | 266.13      | 0.17120      | YES YES         |
| 8 | b2   |          | 267.47      | 0.14718      | YES YES         |
| 9 | b1   |          | 284.98      | 14.17339     | YES YES         |
| 10| a1   |          | 798.95      | 23.52586     | YES YES         |
| 11| b2   |          | 799.27      | 24.53594     | YES YES         |
| 12| a1   |          | 832.81      | 0.04377      | YES YES         |

ROHF-UCCSD(T)/aug-cc-pVTZ(-PP) (C2v - 3B2)

Cartesian coordinates

| Rh | 0.0000000 | 0.0000000 | 0.0001973 |
| 0  | 0.0000000 | 1.4833074 | 0.8560654 |
| 0  | 0.0000000 | -1.4833074 | 0.8560654 |
| 0  | 0.0000000 | 0.0000000 | -1.7123281 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|-----------------|
| 7 | a1   |          | 266.13      | 0.17120      | YES YES         |
| 8 | b2   |          | 267.47      | 0.14718      | YES YES         |
| 9 | b1   |          | 284.98      | 14.17339     | YES YES         |
| 10| a1   |          | 798.95      | 23.52586     | YES YES         |
| 11| b2   |          | 799.27      | 24.53594     | YES YES         |
| 12| a1   |          | 832.81      | 0.04377      | YES YES         |

Table S10. Optimized structures, point groups used for calculations and vibrational data for the Q1 electronic state.

| B3LYP/def2-TZVP (D3h - 5A"1) |

Cartesian coordinates

| Rh | 0.0000000 | 0.0000000 | 0.0000000 |
| 0  | 0.8787980 | -1.5221229 | 0.0000000 |
| 0  | 0.8787980 | 1.5221229  | 0.0000000 |
| 0  | -1.7575961 | 0.0000000 | 0.0000000 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|-----------------|
| 7 | e'   |          | 222.82      | 0.99504      | YES YES         |
| 8 | e'   |          | 222.82      | 0.99504      | YES YES         |
| 9 | a2"  |          | 266.02      | 8.22439      | YES NO          |
| 10| e'   |          | 624.56      | 8.10380      | YES YES         |
| 11| e'   |          | 624.56      | 8.10380      | YES YES         |
| 12| a1'  |          | 780.39      | 0.00000      | NO YES          |

M06L/def2-TZVP (D3h - 5A"1)

Cartesian coordinates

| Rh | 0.0000000 | 0.0000000 | 0.0000000 |
| 0  | 0.8789865 | -1.5240254 | 0.0000000 |
| 0  | 0.8789865 | 1.5240254  | 0.0000000 |
| 0  | -1.7579729 | 0.0000000 | 0.0000000 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|-----------------|
| 7 | e'   |          | 213.37      | 1.07270      | YES YES         |
| 8 | e'   |          | 213.37      | 1.07270      | YES YES         |
| 9 | a2"  |          | 265.06      | 8.22439      | YES NO          |
| 10| e'   |          | 624.56      | 8.10380      | YES YES         |
| 11| e'   |          | 624.56      | 8.10380      | YES YES         |
| 12| a1'  |          | 780.39      | 0.00000      | NO YES          |

ROHF-UCCSD(T)/aug-cc-pVTZ(-PP) (C2v - 5A")

Cartesian coordinates

| Rh | 0.0000000 | 0.0000000 | 0.0000000 |
| 0  | 0.8789865 | -1.5240254 | 0.0000000 |
| 0  | 0.8789865 | 1.5240254  | 0.0000000 |
| 0  | -1.7579729 | 0.0000000 | 0.0000000 |

Vibrational data

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|-----------------|
| 7 | e'   |          | 213.37      | 1.07270      | YES YES         |
| 8 | e'   |          | 213.37      | 1.07270      | YES YES         |
| 9 | a2"  |          | 265.06      | 8.22439      | YES NO          |
| 10| e'   |          | 607.93      | 3.27347      | YES YES         |
| 11| e'   |          | 607.93      | 3.27347      | YES YES         |
| 12| a1'  |          | 776.43      | 0.00000      | NO YES          |
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