**Electronic Supporting Information:**

**Evaluation of the Pr + O → PrO⁺ + e⁻ Chemi-ionization Reaction Enthalpy and Praseodymium Oxide, Carbide, Dioxide, and Carbonyl Cation Bond Energies**

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**Theoretical Calculations**. Theoretical calculations were performed for the ground and low-lying excited states of $Pr^+$ using different basis sets and levels of theory and compared to experimental values to determine which provides the most reliable ground state values for $PrO^+$, $PrC^+$, $PrO_2^+$, and $PrCO^+$. The B3LYP, PBE0, and CCSD(T) levels of theory were used with the ANO and Seg. SDD basis set and the calculated energies for states of $Pr^+$ are summarized in Table S1. Calculated energies, vibrational frequencies, and bond lengths for the ground and low-lying excited states of $PrO^+$, $PrC^+$, $PrO_2^+$, and $PrCO^+$ calculated using these levels of theory and basis sets (along with the 6-311+G(3df) basis sets for C and O) are summarized in Tables S2, S3, S4, and S5, respectively. Additional calculations on the ground state BDEs of $PrO^+$, $PrC^+$, $PrO_2^+$, and $PrCO^+$ were conducted using double- (X=D), triple- (X=T), and quadruple-$\zeta$ (X=Q) correlation consistent all-electron basis sets for Pr, cc-pVXZ-DK3, along with aug-cc-pVXZ-DK basis sets on C and O.

The $PrO^+$ ground state is predicted to be $^3H$ ($[\delta^1\phi^1] \pi^4\sigma^2$) at all levels of theory and basis sets after spin-orbit correction (Table S2). The valence electrons are the 4f and 6s from $Pr^+$ ($^5I$, $4f^3$ $6s^1$) and the four 2p electrons of O ($^3P$, $2p^4$) and they combine to form $\sigma$ and $\pi$ bonding molecular orbitals (MOs) using the 5d orbitals on Pr (2 electrons) and the 2p orbitals on O (4 electrons). The remaining valence electrons are located in the 4f orbitals of Pr (as designated by square brackets). For an internuclear axis along the z direction, the $\pi$ bonding MO arises from the Pr $5d_{xz}$ and $5d_{yz}$ interacting with the O $2p_x$ and $2p_y$ orbitals. The $\sigma$ bonding MO arises from the interaction of the Pr $5d_{z^2}$ orbital with the O $2p_z$ orbital. The theoretical bond length ranges between $1.729 - 1.752$ Å.

The first low-lying excited state of PrO$^+$ is calculated to be the $^3\Gamma$ state ($[\pi^1\phi^1]\,\pi^4\sigma^2$), which lies 0.03-0.29 eV higher than the $^3$H ground configuration. In this configuration as well as all low-lying states with a triplet spin, the bonding MOs are similar to those of the ground state but differ from the multiple occupations of the 4f orbitals by the two non-bonding electrons. In the PrO$^+$ $^5$I ($\pi^4\sigma^1$ $[\pi^1\delta^1\phi^1]$) excited state, one of the bonding electrons is promoted to a 4f orbital, leading to an increase of $2.51 - 3.64$ eV above the ground state. This change is also accompanied by an increase in the bond length to $1.988 - 2.015$ Å and decrease in the vibrational frequency, from 890 - 933 cm$^{-1}$ to 559 - 584 cm$^{-1}$.

For PrC$^+$, the ground state was predicted to be $^5$I ($[\delta^1\phi^1]\,\sigma^1\pi^3$) at all levels of theory and basis sets after spin-orbit corrections, Table S3. However, at the B3LYP/Seg.SDD level, the $^5$H ($[\pi^1\phi^1]\,\sigma^1\pi^3$) is also predicted as the ground state. Additional PrC$^+$ states were located, including $^5$H ($[\pi^1\phi^1]\,\sigma^1\pi^3$), $^5\Phi$ ($[\sigma^1\delta^1]\,\sigma^1\pi^3$), $^5\Pi$ ($[\delta^2]\,\sigma^1\pi^3$), $^7$H ($[\sigma^1\delta^1\phi^2]\,\sigma^1\pi^2$), and $^7\Sigma$ ($[\sigma^1\delta^2]\,\sigma^1\pi^2$), which lie 0.00 - 0.29, $0.37 - 0.57$, $0.43 - 0.62$, $0.04 - 1.09$, and $0.73 - 1.39$ eV above the ground state, respectively.

For PrO$_2^+$, the ground state is predicted to be a linear molecule with a $^3\Phi$ ($[\sigma_u^1\phi_g^1]\,\sigma_g^2\pi_g^4\pi_u^4$) electronic configuration at all levels of theory and basis sets (Table S4). In this configuration (molecule lying along the z axis), the $5d_{z2}$ orbital of Pr$^+$ combines with $2p_z$ orbitals on the O atoms to form a $\sigma_g$ bonding MO, Fig. 9. A bonding set of $\pi_g$ MOs are formed from out-of-phase $2p_x$ and $2p_y$ orbitals on the two O atoms that combine in-phase with the Pr$^+$ $5d_{xz}$ and $5d_{yz}$ orbitals, respectively. Combining the $2p_x$ and $2p_y$ orbitals in-phase with a small amount of 4f character on Pr$^+$ gives largely non-bonding $\pi_u$ MOs. Lastly, there are two electrons in nonbonding Pr 4f orbitals. The first low-lying excited state for linear PrO$_2^+$ is predicted to be the $^3\Delta$ state ($[\sigma_u^1\delta_u^1]\,\sigma_g^2\pi_u^4\pi_g^4$), which lies $0.04 - 0.10$ eV above the ground state. In this configuration, the bonding MOs are similar to those of the ground state but differ in the occupation of the 4f orbitals, as is also true for all low-lying quartet states. Additionally, non-linear OPrO$^+$ species were also explored with the lowest being a $^3$B$_1$ state. This state has an OPrO angle of ~43° and Pr-O bond lengths of 2.00 Å, with an energy 0.67 - 89 eV above the linear $^4$H state.

For the PrCO$^+$ species, a $^5$H ($\pi^4\sigma^2$ [$\sigma^1\delta^1\phi^1$] $\sigma^1$) electronic state is calculated to be the ground state at all levels of theory. Here, the bonding $\pi$ and $\sigma$ valence electrons of C and O are in MOs similar to free carbon monoxide. The calculated CO bond lengths range between 1.114 – 1.122 (Table S5), slightly shorter than the calculated values for free CO: 1.124 and 1.123 at B3LYP and PBE0 levels of theory, respectively. Additional low-lying excited states having electronic configurations of $^5$I ($\pi^4\sigma^2$ [$\pi^1\delta^1\phi^1$] $\sigma^1$) and $^5\Sigma(\pi^4\sigma^2[\sigma^1\delta^2]\sigma^1)$ were calculated and lie 0.07 – 0.40 and 0.56 – 0.72 eV above the ground state, respectively. A $^5$L $\sigma^1\pi^4$ [$\sigma^1\delta^1\phi^1$] $\delta^1$ low-lying excited state was calculated, in which 6s electron has been promoted to a Pr$^+$ 5d atomic orbital. The $^5$L state lies 0.48 – 0.75 eV higher in energy than the $^5$I state and correlates with the $^5$L (4f$^3$5d$^1$) state of Pr$^+$ (promotion energy of 0.565 eV). Other low-lying excited states having 4f$^3$ configurations with triplet multiplicities were also calculated and lie 0.08 – 0.29 eV above the ground state.

**Spin-Orbit Energy Correction.** Determination of the ground state electronic energies for the different metal cation species obtained from the theoretical calculations is complicated by spin-orbit (SO) effects. The theoretical relative energies are averaged over all SO levels, whereas the 0 K BDEs that are measured in the guided ion beam experiments correspond to energy differences between the ground state SO levels of reactants and products. Therefore, a more accurate comparison between theoretical and experimental BDEs can be obtained by employing a semi-empirical approach to estimating the SO splitting, as done previously for third row transition metals, lanthanides, and the actinide thorium.[1-11] For the neutral reactants and Pr$^+$, the SO energy correction to the calculated theoretical energies is obtained from a weighted average of the experimental SO levels. The SO energy corrections for the ground states of Pr$^+$ ($^5$I) and O ($^3$P) are 0.280 eV and 0.010 eV, respectively.[12] For PrO$^+$, PrC$^+$, PrO$_2^+$, and PrCO$^+$, the SO splitting energy is given by E$^{SO}$ = A $\Lambda$ M$_s$, where A is the SO splitting constant, $\Lambda$ is the orbital angular momentum quantum number, and M$_s$ is the spin quantum number for a specific SO level $\Omega$ = $\Lambda$+ M$_s$. E$^{SO}$ is also equal to the summation $\Sigma a_i l_i \cdot s_i$, where $l_i \cdot s_i$ is the dot product of the orbital angular momentum and the spin of electron $i$ and $a_i$ is the SO parameter for the 4f electrons of the neodymium cation $\zeta_{4f}$(Pr$^+$) = 649 cm$^{-1}$.[13]

The first-order SO energy correction for PrO$^+$, PrC$^+$, PrO$_2^+$, and PrCO$^+$ where $\Lambda \neq 0$ can be determined using the values for $\zeta_{4f}$(Pr$^+$) and $E^{SO} = A\,\Lambda\,M_s = \Sigma a_i l_i \cdot s_i$. For example, the $^4$H state of PrO$^+$ splits into $^3$H$_\Omega$ levels with $\Omega$ = 6, 5, and 4, where $^3$H$_4$, with $\Lambda$ = 5 and $M_s$ = -1, is the ground level. Using $\zeta_{4f}$(Pr$^+$) and $E^{SO} = A\,\Lambda\,M_s = \Sigma a_i l_i \cdot s_i$, this ground state lies relative to the SO average value by $E^{SO}$ = A 5 (-1) = (2.5 $a_i$) = -1622 cm$^{-1}$ = -0.201 eV so that A = 324 cm$^{-1}$. The theoretically obtained BDE is then corrected by this SO energy and that for the products. Table S2 – S5 list the SO corrected relative energies for the various electronic states of PrO$^+$, PrC$^+$, PrO$_2^+$, and PrCO$^+$, where SO corrections of 0.201, 0.241, 0.080, and 0.291 eV, respectively, have been used.

**References**

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**Table S1.** Relative energies for the ground and low-lying excited states of Pr⁺ calculated at different levels of theory and basis sets, and ground electronic energies for O, C, and CO calculated at the same levels of theory.

| Species | State | Configuration | Level | Basis set | $s(s+1)^a$ | $E(E_h)$ |
|---------|-------|---------------|-------|-----------|------------|----------|
| Pr⁺ | $^5I$ | $4f^36s^1$ | B3LYP | ANO | 6.00 | -516.774187 |
| | | | | Seg. SDD | 6.00 | -516.774225 |
| | | | | cc-pVDZ-DK3 | 6.00 | -9232.831275 |
| | | | | cc-pVTZ-DK3 | 6.00 | -9232.838792 |
| | | | | cc-pVQZ-DK3 | 6.00 | -9232.841656 |
| | | | PBE0 | ANO | 6.00 | -516.642314 |
| | | | | Seg. SDD | 6.00 | -516.642001 |
| | | | | cc-pVDZ-DK3 | 6.00 | -9232.357922 |
| | | | | cc-pVTZ-DK3 | 6.00 | -9232.364070 |
| | | | | cc-pVQZ-DK3 | 6.00 | -9232.368772 |
| | | | CCSD (T,full) | ANO | 6.00 | -516.382301 |
| | | | | Seg. SDD | 6.00 | -516.328049 |
| | | | | cc-pVDZ-DK3 | 6.00 | -9229.479068 |
| | | | | cc-pVTZ-DK3 | 6.00 | -9229.540957 |
| | | | | cc-pVQZ-DK3 | 6.00 | -9229.562535 |
| | $^5L$ | $4f^35d^1$ | B3LYP | ANO | 6.00 | -516.742984 |
| | | | | Seg. SDD | 6.00 | -516.743015 |
| | | | PBE0 | ANO | 6.00 | -516.616789 |
| | | | | Seg. SDD | 6.00 | -516.616445 |
| | | | CCSD (T,full) | ANO | 6.00 | -516.350201 |
| | | | | Seg. SDD | 6.00 | -516.295960 |

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|---|---|---|---|---|---|---|
| | $^3$I | $4f^36s^1$ | B3LYP | ANO | 3.00 | -516.772181 |
| | | | | Seg. SDD | 3.00 | -516.772177 |
| | | | PBE0 | ANO | 3.00 | -516.639029 |
| | | | | Seg. SDD | 3.00 | -516.638663 |
| | | | CCSD(T,full) | ANO | 3.00 | -516.382403 |
| | | | | Seg. SDD | 3.00 | -516.328137 |
| | $^5$K | $4f^35d^1$ | B3LYP | ANO | 6.00 | -516.742984 |
| | | | | Seg. SDD | 6.00 | -516.743015 |
| | | | PBE0 | ANO | 6.00 | -516.616789 |
| | | | | Seg. SDD | 6.00 | -516.616445 |
| | | | CCSD (T,full) | ANO | 6.00 | -516.350201 |
| | | | | Seg. SDD | 6.00 | -516.295960 |
| O | $^3$P | $2s^22p^4$ | B3LYP | 6-11+G(3df) | 2.00 | -75.090913 |
| | | | PBE0 | 6-11+G(3df) | 2.00 | -75.012913 |
| | | | CCSD (T,full) | 6-11+G(3df) | 2.01 | -74.994166 |
| C | $^3$P | $2s^22p^2$ | B3LYP | 6-11+G(3df) | 2.00 | -37.857471 |
| | | | PBE0 | 6-11+G(3df) | 2.00 | -37.803210 |
| | | | CCSD (T,full) | 6-11+G(3df) | 2.01 | -37.799083 |
| CO | $^1\Sigma^+$ | $1\sigma^22\sigma^21\pi^4$ | B3LYP | 6-11+G(3df) | 0.00 | -113.356792 |
| | | | PBE0 | 6-11+G(3df) | 0.00 | -113.224996 |
| | | | CCSD (T,full) | 6-11+G(3df) | 0.00 | -113.201595 |

[a] * = spin-contaminated state.

**Table S2.** PrO$^+$ energies, bond lengths (Å), vibrational frequencies (cm$^{-1}$, scaled by 0.989) calculated at different levels of theory and basis sets for Pr. Orbitals in brackets are the Pr$^+$ valence 4f electrons and orbitals outside the brackets are the PrO$^+$ bonding orbitals.

| State | Configuration | Level | Pr$^+$ basis set | s(s+1)[a] | E (E$_h$) | Bond length | Vibrational Frequency |
|---|---|---|---|---|---|---|---|
| $^3$H | [δ$^1$φ$^1$] π$^4$σ$^2$ | B3LYP | ANO | 2.01 | -592.120476 | 1.752 | 900 |
| | | | Seg. SDD | 2.01 | -592.121819 | 1.750 | 901 |
| | | | cc-pVDZ-DK3 | 2.02 | -9308.203320 | 1.750 | 896 |
| | | | cc-pVTZ-DK3 | 2.02 | -9308.230774 | 1.748 | 901 |
| | | | cc-pVQZ-DK3 | 2.02 | -9308.233446 | 1.747 | 901 |
| | | PBE0 | ANO | 2.01 | -591.918306 | 1.733 | 931 |
| | | | Seg. SDD | 2.00 | -591.910834 | 1.750 | 901 |
| | | | cc-pVDZ-DK3 | 2.02 | -9307.661210 | 1.732 | 926 |
| | | | cc-pVTZ-DK3 | 2.02 | -9307.686693 | 1.729 | 933 |
| | | | cc-pVQZ-DK3 | 2.02 | -9307.691673 | 1.729 | 932 |
| | | CCSD (T,full)[c] | ANO | 2.01 | -591.669475 | | |
| | | | Seg. SDD | 2.01 | -591.610574 | | |
| | | | cc-pVDZ-DK3 | 2.02 | -9304.760357 | | |
| | | | cc-pVTZ-DK3 | 2.02 | -9304.913575 | | |
| | | | cc-pVQZ-DK3 | 2.02 | -9304.913575 | | |
| $^3$Γ | [π$^1$φ$^1$] π$^4$σ$^2$ | B3LYP | ANO | 2.01 | -592.113522 | 1.759 | 895 |
| | | | Seg. SDD | 2.01 | -592.112573 | 1.758 | 895 |
| | | PBE0 | ANO | 2.00 | -591.911724 | 1.740 | 925 |
| | | | Seg. SDD | 2.01 | -591.911268 | 1.741 | 924 |
| | | CCSD (T,full)[c] | ANO | 2.01 | -591.665593 | | |
| | | | Seg. SDD | 2.01 | -591.611220 | | |

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|---|---|---|---|---|---|---|---|
| $^3\Delta$ | $[\sigma^1\phi^1]\,\pi^4\sigma^2$ | B3LYP | ANO | 2.01 | -592.100177 | 1.758 | 890 |
| | | | Seg. SDD | 2.01 | -592.099575 | 1.758 | 890 |
| | | PBE0 | ANO | 2.01 | -591.899932 | 1.739 | 919 |
| | | | Seg. SDD | 2.01 | -591.898956 | 1.740 | 918 |
| | | CCSD (T,full)[c] | ANO | 2.01 | -591.658761 | | |
| | | | Seg. SDD | 2.01 | -591.604552 | | |
| $^3\Sigma$ | $[\delta^2]\,\pi^4\sigma^2$ | B3LYP | ANO | 2.02 | -591.901303 | 1.745 | 902 |
| | | | Seg. SDD | 2.02 | -591.900600 | 1.745 | 902 |
| | | PBE0 | ANO | 2.02 | -591.652722 | 1.727 | 933 |
| | | | Seg. SDD | 2.02 | -591.900600 | 1.727 | 933 |
| | | CCSD (T,full)[c] | ANO | 2.02 | -591.652722 | | |
| | | | Seg. SDD | 2.02 | -591.598609 | | |
| $^5I$ | $[\pi^1\delta^1\phi^1]\,\pi^4\sigma^1$ | B3LYP | ANO | 6.00 | -592.011326 | 2.015 | 560 |
| | | | Seg. SDD | 6.00 | -592.014183 | 2.015 | 563 |
| | | PBE0 | ANO | 6.00 | -591.807858 | 1.988 | 580 |
| | | | Seg. SDD | 6.00 | -591.807558 | 1.988 | 579 |
| | | CCSD (T,full)[c] | ANO | 6.01 | -591.524577 | | |
| | | | Seg. SDD | 6.01 | -591.468969 | | |
| $^5\Phi$ | $[\delta^2\phi^1]\,\pi^4\sigma^1$ | B3LYP | ANO | 6.00 | -591.979076 | 2.018 | 569 |
| | | | Seg. SDD | 6.00 | -591.979134 | 2.018 | 569 |
| | | PBE0 | ANO | 6.00 | -591.774539 | 1.993 | 584 |
| | | | Seg. SDD | 6.00 | -591.805806 | 1.984 | 579 |
| | | CCSD (T,full)[c] | ANO | 6.01 | -591.521641 | | |
| | | | Seg. SDD | 6.01 | -591.466149 | | |
| $^5\Sigma$ | $[\sigma^1\delta^2]\,\pi^4\sigma^1$ | B3LYP | ANO | 6.00 | -591.992123 | 2.063 | 559 |
| | | | Seg. SDD | 6.00 | -591.992180 | 2.006 | 559 |

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|---|---|---|---|---|---|
| PBE0 | ANO | 6.00 | -591.787460 | 1.978 | 574 |
| | Seg. SDD | 6.00 | -591.787160 | 1.978 | 574 |
| CCSD (T,full) [c] | ANO | 6.01 | -591.510093 | | |
| | Seg. SDD | 6.01 | -591.457303 | | |

[a] * = spin-contaminated state.  [b] $E_{rel}$ values are obtained from zero-point energy corrected energies.

[c] Single point calculations using the PBE0 bond lengths for the same basis set.

**Table S3.** PrC$^+$ energies, bond lengths (Å), vibrational frequencies (cm$^{-1}$, scaled by 0.989) calculated at different levels of theory and basis sets for Pr. Orbitals in brackets are the Pr$^+$ valence 4f electrons and orbitals outside the brackets are PrC$^+$ bonding orbitals.

| State | Configuration | Level | Pr$^+$ basis set | s(s+1)[a] | E (E$_h$) | Bond length | Vibrational Frequency |
|-------|---------------|-------|------------------|-----------|-----------|-------------|-----------------------|
| $^5$I | [$\delta^1\phi^1$] $\sigma^1\pi^3$ | B3LYP | ANO | 6.03 | -554.734616 | 1.986 | 691 |
| | | | Seg. SDD | 6.01 | -554.731029 | 1.981 | 725 |
| | | | cc-pVDZ-DK3 | 6.05 | -9270.795190 | 2.009 | 612 |
| | | | cc-pVTZ-DK3 | 6.02 | -9270.825524 | 1.986 | 707 |
| | | | cc-pVQZ-DK3 | 6.03 | -9270.813021 | 1.999 | 653 |
| | | PBE0 | ANO | 6.02 | -554.562744 | 1.963 | 742 |
| | | | Seg. SDD | 6.02 | -554.562683 | 1.963 | 742 |
| | | | cc-pVDZ-DK3 | 6.01 | -9270.296302 | 1.972 | 742 |
| | | | cc-pVTZ-DK3 | 6.01 | -9270.309395 | 1.965 | 748 |
| | | | cc-pVQZ-DK3 | 6.01 | -9270.298745 | 1.960 | 753 |
| | | CCSD (T,full)[c] | ANO | 6.13 | -554.319921 | | |
| | | | Seg. SDD | 6.13 | -554.267027 | | |
| | | | cc-pVDZ-DK3 | 6.02 | -9267.399409 | | |
| | | | cc-pVTZ-DK3 | 6.07 | -9267.481477 | | |
| | | | cc-pVQZ-DK3 | 6.06 | -9267.505605 | | |
| $^5$H | [$\pi^1\phi^1$] $\sigma^1\pi^3$ | B3LYP | ANO | 6.05 | -554.733637 | 1.997 | 665 |
| | | | Seg. SDD | 6.05 | -554.733922 | 1.998 | 662 |
| | | PBE0 | ANO | 6.03 | -554.561900 | 1.973 | 728 |
| | | | Seg. SDD | 6.01 | -554.555401 | 1.971 | 748 |
| | | CCSD (T,full)[c] | ANO | 6.15 | -554.320730 | | |
| | | | Seg. SDD | 6.02 | -554.262103 | | |

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|---|---|---|---|---|---|---|---|
| $^5\Phi$ | $[\sigma^1\delta^1]\,\sigma^1\pi^3$ | B3LYP | ANO | 6.07 | -554.720415 | 2.006 | 890 |
| | | | Seg. SDD | 6.08 | -554.720475 | 2.008 | 550 |
| | | PBE0 | ANO | 6.01 | -554.548424 | 1.971 | 745 |
| | | | Seg. SDD | 6.01 | -554.548187 | 1.971 | 745 |
| | | CCSD (T,full)[c] | ANO | 6.04 | -554.312701 | | |
| | | | Seg. SDD | 6.04 | -554.259822 | | |
| $^5\Pi$ | $[\delta^2]\,\sigma^1\pi^4$ | B3LYP | ANO | 6.07 | -554.720415 | 2.006 | 570 |
| | | | Seg. SDD | 6.08 | -554.720475 | 2.009 | 547 |
| | | PBE0 | ANO | 6.02 | -554.549894 | 1.971 | 728 |
| | | | Seg. SDD | 6.02 | -554.549680 | 1.971 | 728 |
| | | CCSD (T,full)[c] | ANO | 6.05 | -554.313318 | | |
| | | | Seg. SDD | 6.05 | -554.260440 | | |
| $^7H$ | $[\sigma^1\delta^1\phi^2]\,\sigma^1\pi^2$ | B3LYP | ANO | 12.00 | -554.715916 | 2.336 | 490 |
| | | | Seg. SDD | 12.00 | -554.732276 | 2.336 | 491 |
| | | PBE0 | ANO | 12.00 | -554.559851 | 2.317 | 505 |
| | | | Seg. SDD | 12.00 | -554.560148 | 2.309 | 510 |
| | | CCSD (T,full)[c] | ANO | 12.01 | -554.284826 | | |
| | | | Seg. SDD | 12.01 | -554.229785 | | |
| $^7\Sigma$ | $[\sigma^1\delta^2]\,\sigma^1\pi^2$ | B3LYP | ANO | 12.00 | -554.713360 | 2.329 | 483 |
| | | | Seg. SDD | 12.00 | -554.714009 | 2.327 | 487 |
| | | PBE0 | ANO | 12.00 | -554.542059 | 2.306 | 502 |
| | | | Seg. SDD | 12.00 | -554.542521 | 2.303 | 506 |
| | | CCSD (T,full)[c] | ANO | 12.01 | -554.278690 | | |
| | | | Seg. SDD | 12.01 | -554.237199 | | |

[a] * = spin-contaminated state.

[b] $E_{rel}$ values are obtained from zero-point energy corrected energies.

[c] Single point calculations using the PBE0 bond lengths for the same basis set.

**Table S4.** PrO$_2^+$ energies, bond angles, and bond lengths (Å) calculated at different levels of theory and basis sets for Pr. CCSD(T) calculations use optimized PBE0 structures with scaled PBE0 frequencies for zero-point corrections. Orbitals in brackets are the Pr$^+$ valence 4f electrons and orbitals outside the brackets are the PrO$_2^+$ bonding orbitals.

| State | Configuration | Level | Pr$^+$ basis set | s(s+1)[a] | E (E$_h$) | ∠OPrO (□) | r( |
|---|---|---|---|---|---|---|---|
| $^3\Phi^-$ | $[\sigma_u^1\phi_g^1]\,\sigma_g^2\pi_g^4\pi_u^4$ | B3LYP | ANO | 2.01 | -667.307370 | 180 | |
| | | | Seg. SDD | 2.01 | -667.306971 | 180 | |
| | | | cc-pVDZ-DK3 | 2.00 | -9383.439072 | 180 | |
| | | | cc-pVTZ-DK3 | 2.00 | -9383.482488 | 180 | |
| | | | cc-pVQZ-DK3 | 2.00 | -9383.496913 | 180 | |
| | | PBE0 | ANO | 2.01 | -667.031046 | 180 | |
| | | | Seg. SDD | 2.01 | -667.030329 | 180 | |
| | | | cc-pVDZ-DK3 | 2.00 | -9382.822504 | 180 | |
| | | | cc-pVTZ-DK3 | 2.00 | -9382.865837 | 180 | |
| | | | cc-pVQZ-DK3 | 2.00 | -9382.879581 | 180 | |
| | | CCSD (T,full)[c] | ANO | 2.01 | -666.765705 | | |
| | | | Seg. SDD | 2.01 | -666.710241 | | |
| | | | cc-pVDZ-DK3 | 2.00 | -9379.860822 | | |
| | | | cc-pVTZ-DK3 | 2.01 | -9380.086085 | | |
| | | | cc-pVQZ-DK3 | 2.00 | -9380.068461 | | |
| $^3\Delta$ | $[\sigma_u^1\delta_u^1]\,\sigma_g^2\pi_u^4\pi_g^4$ | B3LYP | ANO | 2.01 | -667.304877 | 180 | |
| | | | Seg. SDD | 2.01 | -667.304214 | 180 | |
| | | PBE0 | ANO | 2.01 | -667.030719 | 180 | |
| | | | Seg. SDD | 2.01 | -667.029925 | 180 | |
| | | CCSD (T,full)[c] | ANO | 2.01 | -666.767023 | 180 | |
| | | | Seg. SDD | 2.01 | -666.711504 | 180 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $^3H$ | $[\delta_u^1\phi_g^1]\,\sigma_g^2\pi_u^4\pi_g^3$ | B3LYP | ANO | 2.01 | -667.231871 | 180 | |
| | | | Seg. SDD | 2.01 | -667.227371 | 180 | |
| | | PBE0 | ANO | 2.01 | -667.028856 | 180 | |
| | | | Seg. SDD | 2.01 | -666.951275 | 180 | |
| | | CCSD (T,full)[c] | ANO | 2.01 | -666.767076 | 180 | |
| | | | Seg. SDD | 2.00 | -666.627485 | 180 | |
| $^3\Sigma$ | $[\delta_u^2]\,\sigma_g^2\pi_u^4\pi_g^4$ | B3LYP | ANO | 2.01 | -667.218120 | 180 | |
| | | | Seg. SDD | 2.01 | -667.215480 | 180 | |
| | | PBE0 | ANO | 2.00 | -666.941025 | 180 | |
| | | | Seg. SDD | 2.01 | -666.940368 | 180 | |
| | | CCSD (T,full)[c] | ANO | 2.01 | -666.673390 | 180 | |
| | | | Seg. SDD | 2.01 | -666.616900 | 180 | |
| $^3A_1$ | $1a_1^2 1b_1^2 2a_1^2 1b_2^2 1a_2^2$ | B3LYP | ANO | 2.02 | -667.285983 | 42.72 | |
| | | | Seg. SDD | 2.02 | -667.285920 | 43.09 | |
| | | PBE0 | ANO | 2.01 | -666.996647 | 42.72 | |
| | | | Seg. SDD | 2.01 | -666.996095 | 42.73 | |
| | | CCSD (T,full)[c] | ANO | 2.00 | -666.729037 | | |
| | | | Seg. SDD | 2.00 | -666.674167 | | |
| $^3B_1$ | $1a_1^2 1b_1^2 2a_1^2 1b_2^2 1a_2^2$ | B3LYP | ANO | 2.00 | -667.284767 | 42.79 | |
| | | | Seg. SDD | 2.01 | -667.285362 | 43.08 | |
| | | PBE0 | ANO | 2.01 | -667.006080 | 42.79 | |
| | | | Seg. SDD | 2.01 | -667.005658 | 42.81 | |
| | | CCSD (T,full)[c] | ANO | 2.00 | -666.734990 | | |
| | | | Seg. SDD | 2.00 | -666.680238 | | |
| $^3A_1$ | $1a_1^2 1b_2^2 1a_2^2 1b_1^2 2b_2^2$ | B3LYP | ANO | 2.02 | -667.247053 | 109.31 | |
| | | | Seg. SDD | 2.02 | -667.246674 | 109.31 | |
| | | PBE0 | ANO | 2.03 | -666.964735 | 109.31 | |

|  |  | Seg. SDD | 2.03 | -666.963927 | 109.31 | |
| CCSD (T,full)[c] | ANO | 2.10 | -666.718635 | | |
|  | Seg. SDD | 2.10 | -666.632352 | | |

[a] * = spin-contaminated state. [b] $E_{rel}$ values are obtained from zero-point energy corrected energies.

[c] Single point calculations using the PBE0 bond lengths for the same basis set.

**Table S5.** PrCO[+] energies and bond lengths calculated at various levels of theory and basis sets. CCSD(T) calculations use optimized PBE0 structures with scaled PBE0 frequencies for zero-point corrections. Orbitals in brackets are the Pr[+] valence 4f electrons and orbitals outside the brackets are the PrCO[+] bonding orbitals.

| | | | | | | | $E_{rel}$ (eV)[b] | |
|---|---|---|---|---|---|---|---|---|
| Configuration | Level | Pr[+] basis set | s(s+1) | E(E$_h$) | r(CO)(Å) | r(MC)(Å) | wo SO | w |
| $\pi^4\sigma^2\,[\sigma^1\delta^1\phi^1]\,\sigma^1$ | B3LYP | ANO | 6.00 | -630.142184 | 1.116 | 3.056 | 0.02 | **0.** |
| | | Seg. SDD | 6.00 | -630.142368 | 1.116 | 3.045 | **0.00** | **0.** |
| | | cc-pVDZ-DK3 | 6.00 | -9346.235867 | 1.118 | 2.997 | | |
| | | cc-pVTZ-DK3 | 6.00 | -9346.235582 | 1.116 | 3.000 | | |
| | | cc-pVQZ-DK3 | 6.00 | -9346.257812 | 1.116 | 3.040 | | |
| | PBE0 | ANO | 6.00 | -629.880919 | 1.114 | 3.001 | **0.00** | **0.** |
| | | Seg. SDD | 6.00 | -629.880794 | 1.114 | 2.990 | **0.00** | **0.** |
| | | cc-pVDZ-DK3 | 6.00 | -9345.590304 | 1.117 | 3.000 | | |
| | | cc-pVTZ-DK3 | 6.00 | -9345.621376 | 1.117 | 3.000 | | |
| | | cc-pVQZ-DK3 | 6.00 | -9345.633250 | 1.117 | 3.000 | | |
| | CCSD (T,full)[c] | ANO | 6.00 | -629.596809 | | | **0.00** | **0.** |
| | | Seg. SDD | 6.00 | -629.542259 | | | **0.00** | **0.** |
| | | cc-pVDZ-DK3 | 6.01 | -9342.682168 | | | | |
| | | cc-pVTZ-DK3 | 6.01 | -9342.707569 | | | | |
| | | cc-pVQZ-DK3 | 6.01 | -9342.839751 | | | | |
| $\pi^4\sigma^2[\pi^1\delta^1\phi^1]\sigma^1$ | B3LYP | ANO | 6.00 | -630.125481 | 1.118 | 2.840 | 0.46 | 0. |
| | | Seg. SDD | 6.00 | -630.125677 | 1.118 | 2.830 | 0.44 | 0. |
| | PBE0 | ANO | 6.00 | -629.865367 | 1.116 | 2.795 | 0.43 | 0. |
| | | Seg. SDD | 6.00 | -629.865268 | 1.116 | 2.781 | 0.43 | 0. |
| | CCSD (T,full)[c] | ANO | 6.00 | -629.585268 | | | | |
| | | Seg. SDD | 6.00 | -629.538845 | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\pi^4\sigma^2[\sigma^1\delta^1\phi^1]\delta^1$ | B3LYP | ANO | 6.00 | -630.116532 | 1.122 | 2.820 | 0.72 | 0. |
| | | Seg. SDD | 6.00 | -630.116257 | 1.117 | 2.988 | 0.72 | 0. |
| | PBE0 | ANO | 6.00 | -629.859050 | 1.119 | 2.781 | 0.60 | 0. |
| | | Seg. SDD | 6.00 | -629.857978 | 1.115 | 2.965 | 0.63 | 0. |
| $\pi^4\sigma^2[\sigma^1\delta^2]\sigma^1$ | B3LYP | ANO | 6.00 | -630.123204 | 1.116 | 3.091 | 0.53 | 0. |
| | | Seg. SDD | 6.00 | -630.123322 | 1.116 | 3.081 | 0.45 | 0. |
| | PBE0 | ANO | 6.00 | -629.862767 | 1.115 | 3.033 | 0.49 | 0. |
| | | Seg. SDD | 6.99 | -629.862560 | 1.114 | 3.020 | 0.49 | 0. |
| | CCSD (T,full) [c] | ANO | 6.00 | -629.583583 | | | 0.36 | 0. |
| | | Seg. SDD | 6.00 | -629.529031 | | | 0.37 | 0. |
| $\pi^4\sigma^1[\pi^1\delta^2\phi^1]\sigma^1$ | B3LYP | ANO | 3.00 | -630.140210 | 1.117 | 2.997 | **0.00** | 0. |
| | | Seg. SDD | 3.00 | -630.140383 | 1.117 | 2.981 | 0.05 | 0. |
| | PBE0 | ANO | 3.00 | -629.877501 | 1.115 | 2.952 | 0.02 | 0. |
| | | Seg. SDD | 3.00 | -629.877362 | 1.115 | 2.936 | 0.01 | 0. |
| | CCSD (T,full) [c] | ANO | 3.01 | -629.596233 | | | 0.02 | 0. |
| | | Seg. SDD | 3.01 | -629.541645 | | | 0.02 | 0.2 |
| $\pi^4\sigma^1[\sigma^1\delta^2\phi^1]\sigma^1$ | B3LYP | ANO | 3.00 | -630.136882 | 1.116 | 3.075 | 0.10 | 0.0 |
| | | Seg. SDD | 3.00 | -630.137021 | 1,116 | 3.063 | 0.14 | 0. |
| | PBE0 | ANO | 3.01 | -629.874241 | 1.114 | 3.024 | 0.18 | 0. |
| | | Seg. SDD | 3.00 | -629.874061 | 1.114 | 3.011 | 0.11 | 0. |
| | CCSD (T,full) [c] | ANO | 3.01 | -629.592891 | | | 0.11 | 0. |
| | | Seg. SDD | 3.01 | -629.538356 | | | 0.11 | 0. |

[a] * = spin-contaminated state.

[b] $E_{rel}$ values are obtained from zero-point energy corrected energies.

[c] Single point calculations using the PBE0 bond lengths for the same basis set.