Abnormal behavior of Cs polyoxides under high pressure

Yuanhui Sun,¹ Dalar Khodagholian,¹ Peter Müller,² Cheng Ji,³ Huiyang Gou,⁴ Richard Dronskowski,²,⁵ Maosheng Miao¹,⁶*

¹Department of Chemistry and Biochemistry, California State University Northridge, CA 91303, USA
²Chair of Solid-State and Quantum Chemistry, Institute of Inorganic Chemistry, RWTH Aachen University, 52056 Aachen, Germany
³Center for High Pressure Science and Technology Advanced Research, Cailun Rd. 1690, Shanghai, China
⁴Center for High Pressure Science and Technology Advanced Research, Beijing 100094, China.
⁵Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, 7098 Liuxian Blvd, Nanshan District, Shenzhen, China
⁶Department of Earth Science, University of California Santa Barbara, Santa Barbara, CA 93106, USA

*Email: mmiao@csun.edu

Abstract

High-pressure can transform the structures and compositions of materials either by changing the relative strengths of bonds or by altering the oxidation states of atoms. Both effects cause unconventional compositions in novel compounds that have been synthesized or predicted in large numbers in the past decade. What naturally follows is a question: what if pressure imposes strong effects to both chemical bonds and atomic orbitals in the same material. A systematic DFT and crystal structure search study of Cs polyoxides under high pressure shows a striking transition of chemistry due to the activation of the Cs 5p core electrons. Opposing to the general trend of polyoxides, the O-O bonds disappear in Cs polyoxides and Cs and O atoms form molecules and monolayers with strong Cs-O covalent bonds. Especially, the abnormal transition of structure and chemical bonds happens to CsO,
a solid peroxide that is stable under ambient pressure, at 221 GPa, which can be accessed by current high-pressure experiments.
Introduction

High-pressure can stabilize compounds with unconventional compositions and containing various homonuclear species such as polycarbon, polynitrogen, polyoxygen and polyhalogen anions, by enhancing the strength of homonuclear bonds. Therefore, it is a general trend that more polyoxides, such as peroxides, superoxides and ozonides that contain stronger O-O bonds become stable under high pressure. On the other hand, high-pressure can also change the composition of stable compounds by altering the relative energies of different atomic orbitals. The most striking phenomenon caused by this effect is the activation of the core electrons in forming new bonds. It is not yet known what will happen if both effects are strong in the same material.

Despite of the strong aspiration, all the previous attempts of achieving core reactivity under ambient pressure have failed due to the ultrahigh stability of the core shells in all elements. The prediction and synthesis of HgF$_4$ attained unusual oxidation state of +4 for Hg and demonstrated the reactivity of 5d semi-core electrons. The obtained HgF$_4$ molecule is not stable and show extremely short lifetime in cryogenic He matrix. In stark contrast, high pressure can stabilize Hg in high oxidations states and form thermodynamically stable HgF$_4$ and HgF$_3$ compounds. More strikingly, as shown by density functional (DFT) calculations, Cs can react with excess amount of F$_2$ under pressure and form stable CsF$_n$ (n>1) compounds consisting of Cs in oxidations states from +2 to +6, which can only occur while its 5p core electrons are activated and form bonds with F.
Regardless of the DFT predictions of CsF\textsubscript{n} (n>1) compounds at pressures that can be readily accessed by the current high-pressure methods, the inevitable damage to the DAC by loading the highly corrosive F\textsubscript{2} liquid obstruct its experimental demonstrations, and the core reactivity of any kind remains as a theory. Among many possible methods to overcome this difficulty, the load of solid, less corrosive, and yet sufficiently strong oxidants is most practical, and the search of such oxidants is an unaccomplished mission of computational high-pressure chemistry. Aiming at this goal, we conducted a full-scale study of Cs polyoxides under pressure, including thorough crystal structure searches of a series Cs\textsubscript{2}O\textsubscript{n} (n=1, 2, ..., 7) compounds in a pressure range from 0 to 500 GPa.

Results and discussion

Stability. Cs-O compounds show distinctly different thermodynamic behaviors below and above 300 GPa (Figure 1). Several Cs\textsubscript{n}O\textsubscript{m} compounds such as CsO, Cs\textsubscript{2}O\textsubscript{3} and CsO\textsubscript{2} are stable under ambient pressure (Figure S1). CsO remains stable up to 500 GPa, the highest pressure that is studied in this work. Remarkably, Cs\textsubscript{2}O\textsubscript{3} becomes unstable at 11.3 GPa but reappears as a stable compound in the pressure range from 346 GPa to 488 GPa. CsO\textsubscript{2} becomes unstable at 346 GPa, whereas new compound with even higher O composition, CsO\textsubscript{3}, becomes stable at 306 GPa. All the compounds are found to be dynamically stable in their stable pressure ranges (Figure S2).

Crystal structures. The most important structural change to Cs-O compounds under high pressure is disappearance of polyoxygen anions that are the key structural component of polyoxides. At 11 GPa, CsO transforms from \textit{Immm} structure\textsuperscript{[17]} into a \textit{P6\textsubscript{3}/mmc} structure in which Cs atoms form a double hexagonal close pack (dhcp) lattice and the O\textsubscript{2}-.
anions occupy one set of the octahedral sites (Figure 2a). The O-O bond length in CsO is 1.432 Å under 100 GPa, which is close to the O-O bond length of 1.460 Å in H₂O₂. It further transforms into a $R\bar{3}m$ structure (Figure 2b) at 221 GPa and an orthogonal structure with $Pnma$ symmetry (Figure 2c) at 429 GPa, respectively. The $R\bar{3}m$ structure can be derived from a CsCl structure by slightly compressing along (111) direction. Both structures show no O-O bond as in typical peroxides, and the minimum O-O distances are 2.538 Å in $R\bar{3}m$ structure at 300 GPa and 2.575 Å in Pnma structure at 500 GPa, respectively. Most strikingly, $R\bar{3}m$ CsO consists of CsO₂ molecules. Half of its Cs atoms (Cs¹) possesses two 1⁰ nearest and six 2⁰ nearest O atoms, and the corresponding Cs-O distances are 1.940 and 2.404 Å at 221 GPa. The other Cs atoms (Cs²) possess two 1⁰ nearest O atoms with a distance of 2.211 Å and six 2⁰ nearest O atoms with a distance of 2.418 Å. Pnma CsO shows no molecular features and all its Cs (O) atoms have six nearest neighbor O (Cs) atoms, with Cs-O distances ranging from 2.092 to 2.175 Å.

The low-pressure structure of Cs₂O₃ ($I\bar{4}3d$) contains O-O bonds, but the high-pressure structure ($Pmmn$, Figure 2d) does not. There are two types of Cs atoms in $Pmmn$ structure, at 400 GPa one (Cs¹) shows slightly shorter Cs-O distances of 1.953, 2.017 and 2.087 Å with 4, 2, and 2 neighboring O atoms, and the other (Cs²) shows Cs-O distances of 2.112, 2.179 and 2.249 Å with 1, 2 and 4 O atoms. Cs¹ and O atoms form a buckled two-dimensional sheet. The Cs superoxide (CsO₂) exhibits O-O bonds throughout its stable pressure range from 0 to 346 GPa. It transforms from the $I4/mmm$ structure at ambient pressure to a C2/m structure (Figure 2e) at 0.5 GPa and shows no further structure change until CsO₂ becomes unstable at 346 GPa. The O-O bond length is 1.351 Å in $I4/mmm$ under ambient pressure and 1.278 Å in C2/m structure under 200 GPa. CsO₃ adopts an $I4/mmm$
structure that contains no O-O bonds (Figure 2f). Instead, its O atoms locate at both tetrahedral centers and square centers of Cs atoms. Correspondingly, the coordination number of Cs is 12 that is one of the highest among all inorganic compounds.

**Electronic structures and the bonding features.** The abnormal disappearance of O-O bonds in Cs polyoxides under high pressure implies a substantial change of the electronic states in these compounds. Both the analysis of the electron states and the calculations of the total charge transfers unveil it is caused by the activation of Cs 5p electrons. The projected density of states (PDOS) shows that the Cs 5p states in a typical peroxide, such as CsO in $P6_3/mmc$ structure, already extend and largely overlap with O 2p states up to the Fermi level under high pressure (Figure 3a). However, the Crystalline Orbital Hamiltonian Population (COHP)\(^{[19]}\) show no bonding between Cs 5p and O 2p (Figure S4), and the total charges calculated in Bader’s Quantum Theory of Atoms in Molecules (QTAIM)\(^{[20]}\) show a typical +1 oxidation state for Cs (Figure 4). On the other hand, COHP calculations show strong covalent O-O bonds in $P63/mmc$ CsO with an integrated COHP (ICOHP) value of -8.964 eV/pair (Table S2). In contrast, $R\bar{3}m$ CsO show strikingly different chemistry, although the compound seems just undergo a structure transformation. Two features of its PDOS (Figure 3b), including reduced gap (also Figure S3) and the large number of 5p states above the Fermi level, reveal the electron transfer from Cs 5p to O 2p states, which is consistent with the Bader charges that clearly show an oxidation state beyond +1 for Cs\(^1\) atoms. Both Electron Localization Function (ELF)\(^{[21]}\) and COHP calculations show strong covalent Cs-O bonds within (CsO\(_2\))^\(-\) anionic molecules (Figure 5 and Figure S4). The ICOHP value of Cs\(^1\)-O bond is -3.319 eV/pair at 221 GPa which is distinctly significant than the ICOHP value of -0.720 eV/pair for the Cs\(^2\)-O bonds. For comparison, the ICOHP
value of Cs-O in $P6_3/mmc$ CsO is -0.709 eV/pair at the same pressure. The $Pnma$ CsO is metallic and the states at the Fermi level show large Cs 5p components, and the Bader charges also show an oxidation state of Cs beyond +1. The ICOHP values for the shortest Cs-O bond is -0.755 eV/pair at 500 GPa (Table S2).

Like $Pnma$ CsO, $C2/m$ CsO$_2$ and $Pmnn$ Cs$_2$O$_3$ are also metallic. However, the states of CsO$_2$ at the Fermi level show only minor contributions from Cs 5p, which is consistent with the low Bader charge of 0.88 e (Figure 4). The low ICOHP values, -0.343 eV/pair, reveal a very weak Cs-O bond, agreeing with a typical superoxide that consist of Cs$^+$ cations and (O$_2^-$) anions. On the other hand, the Bader charges Cs atoms in Cs$_2$O$_3$ reveal a striking multivalent nature of Cs ions. While Cs$^2$ shows a charge of 0.87 at 400 GPa, the Bader charge of Cs$^+$ is as high as 2.17, corresponding to a high oxidation state. Cs$^+$ also form stronger bonds with neighboring O atoms. The ICOHP values of Cs$^+$-O$^-$, Cs$^+$-O$^2$ and Cs$^+$-O$^3$ are -2.507, -1.589, and -1.422 eV/pair. For comparison, the ICOHP values of Cs$^2$-O$^-$, Cs$^2$-O$^2$ and Cs$^2$-O$^3$ are -0.319, -0.540, and -0.565 eV/pair (Table S2). Thus, it proves that Cs$_2$O$_3$ consists of Cs$^+$-O monolayer and isolated Cs$^2$ anions due to the large participation of 5p electrons in Cs$^+$. Correspondingly, the chemical formular of Cs$_2$O$_3$ can be explicitly noted as Cs$^+$(CsO$_3$)$^-$. 

**Pressure-driven core reactivity.** The abnormal behavior of Cs polyoxides under pressure is caused by the activation of Cs 5p electrons and their involvement in forming chemical bonds. Pressure can change the relative energies of different atomic orbitals due to their different size and screening effects of the inner-core orbitals. Most dramatically, it can activate the core electrons if their orbital energies become closer to or even higher than the orbital energies of oxidant atoms, such as F and O. Using a He matrix model, we find
that the energy of Cs 5p orbital becomes higher than that of O 2p orbital at 318 GPa, indicating strong bonding and large electron transfer may occur between the two orbitals (Figure 6). Interestingly, the energy of Ra 5p orbital also crosses with the energy of O 2p orbital at 362 GPa, indicating that Ra polyoxides, such as RaO$_2$[22], might show the same abnormal behavior in the similar pressure range. As a matter of fact, many alkali and alkaline earth metals polyoxides might undergo the same chemical transformations as CsO and Cs$_2$O$_3$. However, the required pressures will be much higher and hard to access by current high-pressure approaches.

**Observing core reactivity in a lab.** The abnormal changes of structure and chemistry of Cs polyoxides provide a unique approach to achieve core reactivity in high-pressure experiment. The major advantage of polyoxides is that many of them can be synthesized as solid samples under ambient pressure and are ready for loading into DAC. Furthermore, despite the dramatic chemical change of the compound, the composition remains the same, eluding the need of reacting two substances in DAC. Among all polyoxides, CsO is the most promising candidate. Solid CsO can be obtained under ambient pressure and load into DAC. Around 221 GPa, it will transform into the $R\bar{3}m$ structure that contains CsO$_2$ molecules bonded by Cs 5p electrons and show a volume reduction (Figure S6). The trade-off of this approach is the requirement of higher pressure around 220 GPa, comparing with the synthesis of Cs polyfluorides under 30 – 50 GPa.[11] Many methods can be used to identify the $R\bar{3}m$ structure, including the direct measurement by XRD (Figure S5) and the measurement of the vibrational modes by IR and Raman spectroscopy. Furthermore, the dramatic change of the band gap can be measured by absorption or emission spectroscopy.

**Conclusion**
DFT calculations and PSO crystal structure searches on a series of Cs-O compounds show striking abnormal changes of Cs polyoxides under high pressure, including the disappearance of O-O bonds, the formation of strong Cs-O covalent bonds, the presence of the multivalent Cs ions, and the exhibition of CsO$_2$ linear molecules and CsO$_3$ monolayers. The electronic structure analysis reveal that the abnormality is caused by the activation of the Cs 5p electrons under high pressure, which renders Cs a p-block element. Many polyoxides can be synthesized under ambient pressure and can be loaded into DAC as solid samples, which provides a new method to observe the core reactivity in high-pressure experiment. Our work shows that CsO is the most promising candidate. It undergoes a structural transition accompanied by the activation of Cs 5p electrons under 221 GPa, which causes many atomic and electronic structure changes that can be detected by various methods such as XRD, IR, Raman etc.
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Figure 1. Stability of Cs-O compounds under high pressure. (a) Enthalpies of formation of Cs$_2$O$_n$ under 100, 200, 300, 400, and 500 GPa, respectively. Solid lines denote the convex hull and dashed lines connect data points. (b) Pressure-composition phase diagram of Cs-O compounds within the estimated pressure range from 0 to 500 GPa.
Figure 2. Crystal structures of Cs-O compounds. (a) CsO in P6\textsubscript{3}/mmc symmetry at 100 GPa. (b) CsO in \textit{R}\text{3}m symmetry at 300 GPa. (c) CsO in Pnma symmetry at 500 GPa. (d) Cs\textsubscript{2}O\textsubscript{3} in Pmmn symmetry at 400 GPa. (e) CsO\textsubscript{2} in C2/m symmetry at 200 GPa. (f) CsO\textsubscript{3} in I4/mmm symmetry at 400 GPa.
Figure 3. Electronic structures of Cs-O compounds. Calculated PDOSs for (a) CsO in P63/mmc symmetry at 221 GPa, (b) CsO in R̅3m symmetry at 221 GPa, (c) CsO in Pnma symmetry at 500 GPa, (d) CsO2 in C2/m symmetry at 200 GPa, (e) Cs2O3 in Pmmm symmetry at 400 GPa, and (f) CsO3 in I4/mmm symmetry at 400 GPa, respectively.
Figure 4. Mechanism of pressure-driven high oxidation states. Calculated Bader charge of Cs in Cs-O compounds in their stable pressure ranges.
Figure 5. Electron localization function of (a) P6$_3$/mmc CsO in the [110] plane at 221 GPa, (b) R3m CsO in the [01-1] plane at 221 GPa, (c) and Pmmm Cs$_2$O$_3$ at 400 GPa, respectively. Isosurface value is 0.5.
Figure 6. Atomic orbital energy levels of the outermost fill $p$ levels of selected elements as a function of pressure, including O, Cs, Ra, and Ba atoms. The energies of O atom are set to zero for given pressures. Pressure effect is modeled by putting elements in a face-centered cubic supercell ($3 \times 3 \times 3$) He matrix, in which one He atom is replaced by the atom being examined. [23]
Supporting information for

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Yuanhui Sun,1 Dalar Khodagholian,1 Peter Müller,2 Cheng Ji,3 Huiyang Gou,4 Richard Dronskowski,2,5 Maosheng Miao1,6*

1Department of Chemistry and Biochemistry, California State University Northridge, CA 91303, USA
2Chair of Solid-State and Quantum Chemistry, Institute of Inorganic Chemistry, RWTH Aachen University, 52056 Aachen, Germany
3Center for High Pressure Science and Technology Advanced Research, Cailun Rd. 1690, Shanghai, China
4Center for High Pressure Science and Technology Advanced Research, Beijing 100094, China.
5Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, 7098 Liuxian Blvd, Nanshan District, Shenzhen, China
6Department of Earth Science, University of California Santa Barbara, Santa Barbara, CA 93106, USA

*Email: mmiao@csun.edu
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1. Computational methods in detail

**Structure search.** Searching for the structures of Cs-O compounds were carried out based on a global minimum search of the free energy landscape with respect to structural variations by combining particle swarm optimization (PSO) algorithm with first-principles energetic calculations.\(^{[1,2]}\) To find the structures that realize the high oxidation state of Cs atoms, we performed global structure searches on O-rich compounds with various Cs\(_2\)O\(_n\) (\(n = 1-7\)) compositions at 0 K and the selected pressures of 100, 200, 300, 400, and 500 GPa, respectively. In addition, the known O-rich Cs-O compounds are included and their energies are compared with structure search results.\(^{[3-6]}\) By evaluating the total energy of these structures, 60% of them with lowest enthalpies together with 40% newly generated structures are regarded as the next generation of structures by the structure operators of PSO. The procure stopped after 20 generations are created. Numerous works using this code show high accuracy and efficiency.\(^{[7-9]}\)

**Electronic structure calculations.** We conducted calculations on the formation enthalpies and electronic properties using density-functional-theory (DFT) as implemented in Vienna \textit{ab initio} simulation package (VASP) code.\(^{[10]}\) The DFT calculations were performed using a generalized gradient approximation\(^ {\text{[11]}}\) exchange-correlation functional within the framework of Perdew-Burke-Ernzerhof density functional.\(^{[12]}\) The projector augmented wave\(^{[13]}\) method was used as a pseudopotential approach with 5\(p^66s^1\) and 2\(s^22p^4\) valence electrons for Cs and O atoms respectively. We adopted a kinetic energy cutoff of 520 eV for wave-function expansion and a \(k\)-point mesh of \(2\pi \times 0.03 \text{ Å}^{-1}\) or less for Brillouin zone integration. The structures (including lattice parameters and atomic positions) were fully optimized until the residual forces were converged within 0.02 eV/Å. The dynamical stability
of predicted structures was determined by phonon calculations using the finite displacement approach\textsuperscript{[14]} as implemented in the Phonopy code.\textsuperscript{[15]} Crystal orbital Hamilton population (COHP) analysis giving information on the interatomic interaction is implemented in the LOBSTER package.\textsuperscript{[16,17]}

**Formation enthalpy calculations.** Formation enthalpy was used to learn the stability of Cs-O compounds, which is calculated by the following formula:

\[
h_f(\text{Cs}_2\text{O}_n) = \left[H(\text{Cs}_2\text{O}_n) - H(\text{Cs}_2\text{O}) - \frac{(n-1)H(O_2)}{2}\right]/(n + 2) \quad (1)
\]

The formula shows formation enthalpy is equal to the differences between sum of enthalpies of products and enthalpies of reactants in reaction \( \text{Cs}_2\text{O} + \frac{n-1}{2}O_2 \rightarrow \text{Cs}_2\text{O}_n \).

Thanks to the exceedingly stability of \( \text{Cs}_2\text{O} \) throughout the studied pressure range, using \( \text{Cs}_2\text{O} \) as a reactant and the above reaction will not change the convexity, i.e. a compound that is shown stable/unstable using the reaction enthalpy as defined above will also be shown stable/unstable if the enthalpy of formation, which is the enthalpy change of the reaction \( 2\text{Cs} + \frac{n}{2}O_2 \rightarrow \text{Cs}_2\text{O}_n \), is used to construct a convex hull. The predicted structure with the lowest enthalpy for each composition is used to evaluate the formation enthalpy with respect to the most stable \( \text{Cs}_2\text{O} \) and \( O_2 \) molecule. \( h_f \) is the formation enthalpy per atom. For the solid lines in Figure 1a, the compounds located on the convex hull are stable against decomposition, because decomposing into other compounds will cost energy.\textsuperscript{[18]}

2. **Thermal and phonon stability of Cs-O compounds**
Figure S1. Enthalpies of formation of Cs$_2$O$_n$ under 0 GPa.
**Figure S2.** Phonon spectrum of (a) CsO in $P6_3/mmc$ symmetry at 100 GPa. (b) CsO in $R3m$ symmetry at 300 GPa. (c) CsO in Pnma symmetry at 500 GPa. (d) Cs$_2$O$_3$ in Pmmm symmetry at 400 GPa. (e) CsO$_2$ in C2/m symmetry at 200 GPa. (f) CsO$_3$ in I4/mmm symmetry at 400 GPa.
3. **Electronic properties of Cs-O compounds**

**Figure S3.** Band structures of (a) P63/mmc CsO and (b) $R\bar{3}m$ CsO under 221 GPa, respectively.
4. **Bonding analysis of Cs-O compounds**

![COHP plots for Cs-O and O-O interactions in CsO under 221 GPa](image)

**Figure S4.** Integrated crystal orbital Hamiltonian population of (a) P6/mm CsO and (b) R3m CsO under 221 GPa, respectively.
5. **Experimental methods to identify Cs-O compounds**

![XRD Patterns Diagram](image)

**Figure S5.** The simulated XRD patterns of CsO in P63/mmc symmetry, CsO in $R\bar{3}m$ symmetry, CsO in Pnma symmetry, Cs$_2$O$_3$ in Pmmm symmetry, CsO$_2$ in C2/m symmetry, and CsO$_3$ in I4/mmm symmetry.
Figure S6. The simulated equation of states of CsO in $P6_3/mmc$ symmetry, CsO in $R\bar{3}m$ symmetry, CsO in $Pnma$ symmetry, $Cs_2O_3$ in $Pmmn$ symmetry, $CsO_2$ in $C2/m$ symmetry, and $CsO_3$ in $I4/mmm$ symmetry.
6. **Structural information of stable Cs-O compounds**

Table S1. Calculated structural parameters of various stable Cs-O compounds.

| Compound | Space group | Lattice parameters (Å, °) | Atomic coordinates (fractional) |
|----------|-------------|---------------------------|---------------------------------|
| CsO (100 GPa) | P6₃/mmc | a = b = 4.3029, c = 6.2159, α = β = γ = 90.0000 | Cs 0.6667, 0.3333, 0.7500, Cs 0.0000, 0.0000, 0.0000, O 0.3333, 0.6667, 0.8652 |
| CsO (300 GPa) | R₃m | a = b = c = 3.5399, α = β = γ = 67.7178 | Cs 0.0000, 0.0000, 0.0000, Cs 0.5000, 0.5000, 0.5000, O 0.2356, 0.2356, 0.2336 |
| CsO (500 GPa) | Pnma | a = 3.1378 | Cs 0.2500, 0.8677, 0.1772, O 0.7500, 0.6385, 0.9654 |
| Cs₂O₃ (400 GPa) | Pmmm | a = 5.7363, b = 4.1196, c = 3.0980, α = β = γ = 90.0000 | Cs 0.3576, 0.5000, 0.0000, Cs 0.0491, 0.0000, 0.0000, O 0.2787, 0.7671, 0.5000, O 0.5828, 0.5000, 0.5000 |
| CsO₂ (200 GPa) | C2/m | a = 6.6226, b = 5.4464, c = 3.0003, α = γ = 90.0000, β = 108.0569 | Cs 0.6984, 0.0000, 0.9446, O 0.9409, 0.1805, 0.6328 |
| CsO₃ (400 GPa) | I₄/mmm | a = b = 2.9398, c = 5.4361, α = β = γ = 90.0000 | Cs 0.5000, 0.5000, 0.5000, O 0.0000, 0.0000, 0.5000, O 0.5000, 0.0000, 0.7500 |
## 7. Integrated crystal orbital Hamiltonian population of Cs-O compounds

**Table S2.** ICOHPs for the nearest neighboring Cs-Cs, Cs-O, and O-O pairs for Cs-O compounds under pressure.

| Space group  | Atomic pairs | Distance (Å) | ICOHP (eV/pair) |
|--------------|--------------|--------------|-----------------|
| CsO (221 GPa) P6\textsubscript{3}/mmc | Cs-Cs | 2.735 | -0.187 |
| | Cs-O | 2.202 | -0.709 |
| | O-O | 1.432 | -8.964 |
| CsO (221 GPa) R\textsuperscript{3}m | Cs-Cs | 2.729 | -0.260 |
| | Cs\textsuperscript{1}-O | 1.940 | -3.319 |
| | Cs\textsuperscript{2}-O | 2.211 | -0.720 |
| | O-O | 2.538 | 0.026 |
| CsO (500 GPa) Pnma | Cs-Cs | 2.594 | -0.284 |
| | Cs-O | 2.092 | -0.755 |
| | O-O | 2.575 | 0.029 |
| Cs\textsubscript{2}O\textsubscript{3} (400 GPa) Pmmn | Cs-Cs | 2.716 | -0.226 |
| | Cs\textsuperscript{1}-O | 1.953 | -2.507 |
| | Cs\textsuperscript{2}-O | 2.111 | -0.540 |
| | O-O | 1.988 | -0.085 |
| CsO\textsubscript{2} (200 GPa) C2/m | Cs-Cs | 4.016 | -0.164 |
| | Cs-O | 2.314 | -0.343 |
| | O-O | 1.278 | -13.632 |
| CsO\textsubscript{3} (400 GPa) I4/mmm | Cs-Cs | 3.422 | -0.116 |
| | Cs-O | 2.002 | -1.954 |
| | O-O | 2.002 | -0.124 |
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