Xenon Suboxides Stable under Pressure

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ABSTRACT: We present results from first-principles calculations on solid xenon–oxygen compounds under pressure. We find that the xenon suboxide XeO2 is the first compound to become more stable than the elements, at around P = 75 GPa. Other, even more xenon-rich compounds follow at higher pressures, while no region of enthalpic stability is found for the monoxide XeO. We establish the spectroscopic fingerprints of a variety of structural candidates for a recently synthesized xenon–oxygen compound at atmospheric pressure and, on the basis of the proposed stoichiometry XeO2, suggest an orthorhombic structure that comprises extended sheets of square-planar-coordinated xenon atoms connected through bent Xe–O–Xe linkages.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory

The chemical reactivity of the “noble” gas xenon has been an active research area over several decades, initially focusing on molecular compounds. In 1962, Bartlett synthesized the first xenon charge-transfer compound, Xe+(PtF6)−1, followed shortly thereafter by syntheses of xenon fluoride2−6 and oxide7−10 compounds, both in molecular and solid form. Recently, Brock and Schrobilgen announced the formation of another, presumably extended, xenon–oxygen compound.11 On the basis of Raman spectroscopy data, they argued that their new compound featured Xe–O bonds, was an extended network, and was probably of stoichiometry XeO2. However, its structure was not resolved. Subsequently, a computational study on potential high-pressure phases of xenon and oxygen found a sequence of XeOx (n ≥ 1) compounds to be stabilized at pressures P > 80 GPa.12 Xenon’s reactivity at high pressures is of major interest because of the “missing xenon” problem,13−15 which regards a seemingly deplete xenon reservoir in our atmosphere compared to expectations from interstellar abundance ratios of the elements. One possible solution is that the “missing” atmospheric xenon is instead bound in mineral or other form within the Earth.16−20 The search for xenon compounds stabilized by pressure has developed into an active field.21−24

Here, we present results from a computational study on xenon oxides under pressure, in particular, investigating xenon-rich compounds. We combine first-principles density functional calculations with the evolutionary algorithm approach to find suitable candidate structures at various pressures. Crystal structure prediction based on evolutionary algorithms25 has been used successfully in the recent past to identify high-pressure phases of known compounds26,27 or to reveal completely new compounds that are unstable at atmospheric pressure.28−30 Other methods to screen the crystal configuration space, based on the particle swarm optimization method31 or random structure searching,32 have been equally successful in their predictions, many of which have eventually been confirmed by experiment.33−35 Here, we find that with increasing pressure, Xe2O3 is the first xenon oxide compound more stable than the elements. We find XeO2 to be stable at pressures P > 75 GPa; its structure is an intriguing composition of one-dimensional XeO chains intercalated with free xenon atoms. We also find a series of more xenon-rich compounds with very similar structural features, which are either stable themselves or at least close to global stability. Our findings imply that xenon monoxide, XeO, has no region of stability up to a pressure of at least P = 200 GPa. We then proceed to attempt to resolve the metastable phase synthesized by Brock and Schrobilgen, based on the candidate structures of various stoichiometry obtained at high pressures. We compare their spectroscopic fingerprints to experimental vibrational data and propose that if the synthesized phase is indeed XeO2, an orthorhombic phase of Pbcn symmetry with extended Xe–O sheets would be its most likely structure.

We summarize the relative ground-state enthalpies of the most competitive xenon oxide compounds in the convex hull plot of Figure 1 as a function of chemical
composition. There, we present the enthalpy of formation per atom, \( \Delta H_f(Xe_nO_m) = (H_f(Xe_nO_m) - mH_f(Xe) - nH_f(O))/(m + n) \). In our ground-state calculations, we approximate the enthalpy of formation by the free energy, \( H_f \approx F = E + pV \). Each point on the convex hull plot denotes a phase stable against decomposition into the elements or other binary compounds, whereas all points above the hull are metastable, exhibiting an exothermic decomposition reaction. Figure 1 shows that at low pressures, no stable xenon oxides exist; that is expected. At \( P = 75 \) GPa, we find the first xenon oxide to become stable against the elements, the suboxide \( Xe_7O_2 \). We find several other xenon suboxides (\( Xe_2O \) and \( Xe_6O_2 \)) to become stable at a similar pressure. The stability of \( Xe_7O_2 \) means that xenon monoxide, \( XeO \), is metastable toward the elements, the suboxide \( Xe_3O_2 \), and pure xenon.

What is the nature of this stabilization? We analyzed the projected atomic charges based on Bader analysis are included in Figure 2. They show our structural interpretation of the formation of \( XeO_2 \) chains, with large positive/negative partial charges on xenon/oxygen. The free xenon atoms in \( Immm-Xe_2O_2 \) carry a charge of +0.23 electrons, which means that this compound features both strong ionic \( Xe-O \) bonding within the chains and weaker ionic \( Xe-O \) bonding involving the “free” xenon atoms. If the xenon content is increased, the partial charge on the free xenon atoms decreases. Most clearly visible in \( Xe_2O_2 \), the xenon partial charge correlates with the distance to the nearest oxygen atoms. In fact, in \( Xe_2O_2 \), xenon atoms farthest away from the \( XeO_2 \) chains are quasi-neutral, and thus, one could expect a segregation into pure xenon and a more oxygen-rich compound to be enthalpically beneficial. A close inspection of the convex hulls in Figure 1 shows that \( XeO_2 \) is actually on the border of instability; it is very close but just above the convex hull. It might be beyond the accuracy of our calculations to decide whether or not \( Xe_7O_2 \) is in fact stable; it could be the most xenon-rich compound that can reasonably form with isolated \( XeO_2 \) chains, which seem to be the dominant structural feature in the most stable xenon-rich compounds that we found.

The presence of two different xenon species, formally \( Xe^{4+} \) and \( Xe^0 \), in these compounds allows for a different...
interpretation, namely, that Xe0 acts as a Lewis base21 and terminal ligand to a cationic center, Xe4+. This bonding mechanism has so far been observed with the cations of gold and mercury only,44−46 with metal−xenon bond lengths of \( d_{\text{M-Xe}} = 2.61−2.77 \) Å. Here, the shortest Xe4+−Xe0 separations (at \( P = 100 \) GPa) are \( d = 2.97−3.05 \) Å; there are eight of them per Xe4+ in each structure. However, the shortest O−Xe0 separations are \( d = 2.57−2.63 \) Å; therefore, the xenon suboxides could be seen as an example of Lewis base stabilization of the Lewis acid XeO2.

We further analyzed the bonding in Xe3O2 by studying the electron localization function (ELF),47 which should give an indication of the presence of both covalent bonds and filled lone pairs. As seen in Figure 3, we essentially found the latter, the filled 5p lone pair on Xe4+ and the 2p lone pairs of O2−. The ELF along the O−Xe separation, both within the XeO2 chains and toward the nearest free xenon atoms, shows no intermediate maxima. The ELF around the free xenon atoms themselves is by all accounts spherical, indicating the absence of covalent interactions with other atoms and thus re-enforcing the picture of an ionic contribution to the overall bonding.

If the XeO2 chains are nominally negatively charged, one could expect interesting electronic properties. Calculations with the hybrid HSE06 functional (including 25% screened exact exchange)48 show that Immm-Xe2O2 has a relatively small electronic band gap, \( \sim 0.1 \) eV at \( P = 100 \) GPa (using the semilocal PBE approximation for the exchange−correlation energy, we obtain a vanishing band gap). Figure 4 shows the electronic density of states (DOS) of Immm-Xe2O2, including projections of the DOS onto spherical atomic components. The valence and conduction bands from −12 to +5 eV are dominated by p electrons of oxygen and xenon, indicating a partial charge transfer from xenon to oxygen; empty bands of Xe p character attest to xenon’s cationic state, in particular, for the in-chain atoms; and empty O p bands show that the charge transfer to oxygen does not fill the O-2p orbitals completely. A lower valence band, from −26 to −15 eV, is made up of the filled s orbitals of both oxygen and xenon.

Because we have found a wide array of xenon oxide compounds stable at high pressures, can we hazard a guess which of those (if any) was made as a metastable compound by Brock and Schrobilgen? We relaxed all xenon oxide candidate structures at \( P = 1 \) atm and, choosing the least unstable phase for each stoichiometry, determined their zone-center phonon frequencies; we attempted to avoid quasi-segregated phases with well-separated xenon atoms and O2 molecules. In Figure 5,
in excess of 13% of the respective frequencies (see the SI for details).

Note that all xenon oxide phases are metastable at $P = 1$ atm with respect to decomposition into pure xenon and oxygen, as indicated by positive enthalpies of formation in Figure 5. In fact, the proposed $\text{XeO}_2$ structure of $P\text{bca}$ symmetry is quite unstable. We cannot rule out that other metastable structures, with lower formation enthalpies, exist. However, $\text{XeO}_2$-$P\text{bca}$ is on energetic grounds our best candidate for the phase synthesized by Brock and Schrobligen, provided that its overall stoichiometry is $\text{XeO}_2$. This structure (see Figure 5) would confirm suggestions by the experimental group; it is a $\text{Xe}\cdots\text{O}$ network structure, with locally quasi-square-planar-coordinated xenon atoms, connected via bent $\text{Xe}\cdots\text{O}\cdots\text{Xe}$ linkages. Globally, the $P\text{bca}$ phase forms stacks of kinked layers of $\text{XeO}_2$. The local environment of each xenon atom has lower symmetry ($C_i$) than suggested by the experimental group ($D_{2d}$). We arrived at this structure (which is the $\text{AgF}_2$ structure type$^{49}$) by assuming the $I4/mmm$-$\text{XeF}_2$ structure type$^{50,51}$ for $\text{XeO}_2$ and following its dynamical instabilities. Intralayer $\text{Xe}\cdots\text{O}$ separations are 2.13–2.2 Å, while shortest interlayer $\text{Xe}\cdots\text{O}$ separations are 3.43 Å. The $P\text{bca}$ phase has an electronic band gap of 1.7 eV in our hybrid-DFT calculations with the HSE06 functional and hence could well explain the yellow color seen in experiment, which suggests absorption at around 2 eV.

It is possible that the highest experimental Raman modes correspond to overtones of fundamental modes (although these have usually an order of magnitude smaller intensity than fundamental modes and therefore may not support this assumption$^{52,53}$); for instance, the intense mode at 570.3 cm$^{-1}$ is at almost exactly twice the frequency of the next mode, seen at 283.9 cm$^{-1}$; that ratio remains close to 2.0 for different oxygen isotopes.$^{11}$ A similar fundamental mode for the highest observed Raman mode would be located at 316 cm$^{-1}$; experimental data show a broad shoulder at that frequency. If this were the correct interpretation of the Raman data, we would look for phases that best fit the lower-frequency Raman modes, ignoring the two highest modes. Even so, various phases (and stoichiometries) could fit the experimental data. If the overall stoichiometry is assumed to be indeed $\text{XeO}_2$, we want to compare experimental data with the metastable $\text{XeO}_2$-$P\text{bca}$ phase; it has Raman-active modes at or near most of the experimental Raman modes (the bar for the twin peak at 228/239 cm$^{-1}$). The complete vibrational spectrum is given in Table 1. Due to the presence of two distinct $\text{XeO}_2$ sheets in the unit cells, all modes are split into pairs. Raman-active modes at 91/103, 195/201, and 297–304 cm$^{-1}$ correspond well to experimental peaks, with the latter potentially providing an overtone signal at around 600 cm$^{-1}$. However, other calculated modes at 390/394 and 464/468 cm$^{-1}$ were not observed in experiment. Calculating the Raman intensities is beyond our computational resources; therefore, a visual analysis of the different modes was performed, which resulted in the assignments given in Table 1. The highest Raman-active modes (464/468 cm$^{-1}$) correspond to symmetric $\text{Xe}\cdots\text{O}$ stretches of each $\text{XeO}_4$ unit; the modes at 390/394 cm$^{-1}$ relate to asymmetric $\text{Xe}\cdots\text{O}$ stretches; the modes at 301/304 and 297/298 cm$^{-1}$ are librations of $\text{XeO}_4$ units within the sheets, roughly around the crystalline $a$ and $b$ axes, respectively; the modes at 195/201 cm$^{-1}$ are $\text{O}\cdots\text{Xe}\cdots\text{O}$ bends within the $\text{XeO}_2$ unit; and the lowest mode pair at 91/103 cm$^{-1}$ relates to librations of $\text{XeO}_4$ units perpendicular to the sheet plane, that is, roughly along the crystalline $c$ axis. We therefore find that the lower-frequency modes seen in experiment agree well with calculated collective motions of the $\text{XeO}_4$ units, whereas the highest calculated modes in this $\text{XeO}_2$ network structure have much lower frequencies than the highest experimental modes. This discrepancy can certainly not be overcome with a rigid scaling factor, and the search for a structure that features the seemingly required much stiffer $\text{Xe}\cdots\text{O}$ bonds might have to continue.
In summary, we have presented results from a computational study on xenon oxides under pressure, concentrating on the xenon-rich side of the binary phase diagram. We find that, on the basis of ground-state enthalpy considerations, the xenon suboxide XeO₂, in an orthorhombic Immm structure, should be the first xenon oxide compound to be more stable than the elements, at around P = 75 GPa. Other xenon-rich compounds follow to become stable at higher pressures. All of these share the common structural feature of XeO₂ chains with intercalated free xenon atoms. Small charge transfer from the free xenon atoms to the XeO₂ chains helps stabilize the compounds. XeO₂ has a very small band gap in its region of stability. Its presence involves the Xe−O molecular stretches. The search for the structure by Brock and Schrobligen might not be finished.

**COMPUTATIONAL DETAILS**

We performed density functional theory calculations as implemented in the VASP package using a plane wave basis set (cutoff energy Eₖ = 600 eV) and the standard projector-augmented wave (PAW) data sets for the elements to model the electron−ion interaction. The electron−electron interaction was modeled within the generalized gradient approximation to the exchange−correlation energy functional. Brillouin zone integrations were performed on regular grids of k-points with a density of 20 per Å⁻¹ for insulating and 40 per Å⁻¹ for small-gap or metallic systems. Electronic DOSs were evaluated using sufficiently denser k-point grids. We used the evolutionary algorithm approach as implemented in the XtalOpt package to predict candidate structures of the desired composition at specific pressures (100, 120, and 150 GPa and 2−4 formula units per unit cell) and reoptimized the structures. The phonon dispersion, and DOS of various phases, and benchmark calculations of DFT-PBE for vibrational properties of noble gas compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

**ASSOCIATED CONTENT**

Supporting Information

Crystal structure information on xenon oxide phases, relative enthalpies of candidate structures as a function of pressure, phonon dispersion, and DOS of various phases, and benchmark calculations of DFT-PBE for vibrational properties of noble gas compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Computational resources provided by the U.K. National Supercomputing Service through the UKCP consortium and funded by EPSRC Grant EP/K013564/1 are gratefully acknowledged.

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