Noble Gases in Solid Compounds Show a Rich Display of Chemistry With Enough Pressure

Maosheng Miao

Department of Chemistry and Biochemistry, California State University Northridge

Abstract

In this review, we summarize the rapid progress of noble gas chemistry in solid compounds under high pressure. Thanks to the recent development of first principles crystal structure search methods, many new noble gas compounds have been predicted and some have been synthesized. Strikingly, almost all types of chemical roles and interactions are found or predicted in these high-pressure noble gas compounds, ranging from cationic and anionic noble gases to covalent bonds between noble gas atoms, and to hydrogen bond-like noble gas bonds. Besides, the recently discovered He insertion reactions reveal a unique chemical force that displays no local chemical bonding, providing examples that noble gas reaction can advance the frontier of chemistry at the very basic level.

Introduction

In many years after their discovery, noble gases (NG) are known as elements that do not have any chemistry. This idea was consolidated by the atomic shell structure and the corresponding theory that all elements are destined to a complete shell while forming compounds. Therefore, the noble gases would remain chemically inert (noble) since their valence orbitals are already completely filled. This doctrine was first challenged in 1933 by Pauling who predicted the formation of KrF₆ and XeF₆ compounds.¹ It took almost another 30 years before the first noble gas compound, XePtF₆ was synthesized by Neil Bartlett.² Soon after, many Xenon binary compounds such as XeF₄, XeF₂ etc. were obtained.³ Till now, there are already a few hundred known noble gas compounds and the list continues to grow.⁴ The most recent advancements include the first truly bonded Argon compound, HArF,⁵ and a striking compound AuXe₄ (Sb₂F₁₁)⁶ in which Xenon, a noble gas element, bonds with Au, a noble metal, as a weak reducing and coordinating agent.

A scenario of rich chemistry for NG elements is rolled out gradually in the past decades, especially while locking them in an extreme chemical environment. For example, many NG elements can be coerced to form charged or strongly polarized species, such as HHe^+ ,⁷ HNGO⁻,⁸ and $HeOLi_2F_2^{9}$ etc. In contrast, similar chemical environment is difficult to achieve in solid compounds since the charge neutrality needs to be preserved globally and locally. As a result, the chemical roles that NG elements can play in solid compounds are more limited. Lots of noble gas compounds are not formed by local chemical bonds featuring electron sharing or transfer. In many of these compounds, noble gases are either bonded to other atoms by weak interactions such as van der Waals force or inserted into the voids preexisting in some solid compounds such as XeF_2 , XeO_3 , etc. noble gases act like reductants (electron donors).

On the other hand, we can drive chemical interactions to an extreme in solid compounds by applying mechanical pressures so that new chemistry can emerge. Due to both the development of first-principles computer simulations^{12,13} and the diamond anvil cell (DAC) experiments,¹⁴ numerous novel compounds have been predicted and some have been synthesized. These new compounds under pressure, such as Na_mCl_n ,¹⁵ H₃S,¹⁶ LaH_n,¹⁷ CsF_n¹⁸ etc, show a distinct trend of having a large range of compositions, with very different stoichiometries to the ambient condition. Although many unconventional stoichiometries are caused by the formation of homonuclear bonds or species, such as Cl-Cl in NaCl₃, some compounds with atypical compositions are formed due to the change of oxidation states of their constituent elements.¹⁹ In some extreme cases, the core electrons, such as the 5p electrons of Cs, can be coerced to form chemical bonds, leading to the formation of atypical compounds, such as CsF₃ and CsF₅.¹⁸

For the same reason, pressure can greatly enrich noble gas chemistry. It goes far beyond the known NG compounds formed by sharing their closed-shell electrons with strong oxidants such as F. In contrast to molecular and ionic species, most of the solid NG compounds under pressure are thermodynamically stable. In this review, we will show that NG elements, under high-pressure can 1) be oxidized by elements such as Fe that usually are not considered as oxidants, 2) become an oxidant themselves and behave like anions in compounds, 3) form strong NG-NG covalent bonds, 4) form intermolecular NG bonds that are similar to hydrogen bonds, 5) form stable compounds that are not bound by any local chemical bonds.

Methods and the progress of high-pressure chemistry

The progresses of high-pressure chemistry strongly depend on the development of experimental methods. The first leap of this field is triggered by the development of diamond anvil cell (DAC) and the corresponding heating and measurement techniques. However, high-pressure experiments are usually very difficult, expensive, and time-consuming. Recently, the density functional theory (DFT) calculations are widely used in predicting phase diagrams of binary compounds under pressure, which gave rise to the second leap of high-pressure chemistry. These "complete ab initio" studies neither use any empirical parameters for electronic structure nor take any crystal structures and chemical bonding information as input. Instead, crystal structures are generated and the globally stable structures are searched, using various algorithms, such as random search (RS),²⁰ genetic algorithm (GA),^{21,22} and particle swarm optimization (PSO).²³ In the last decade, numerous new compounds have been predicted by this method without any experimental input and many of them have been confirmed by DAC experiments. Many of these compounds assume atypical compositions, such as NaCl₃, CsF₃, H₃S, LaH₁₀ etc. The change of the chemistry and the formation of a plethora of atypical compounds can be roughly grouped into two kinds: those caused by the formation of homonuclear bonds and those caused by the change of oxidation states, both of which can be found in high-pressure noble gas compounds.¹⁹

Noble gas chemistry under high pressure

2.1 Oxidation of NG under pressure

Although most part of noble gas chemistry is about the sharing of their closed-shell electrons, oxidizing NG is not an easy task and most of the stable NG compounds contain F, the strongest oxidant element. Several Xenon oxides exist but they are not stable.^{24,25} Pressure can greatly extend the chemistry of NG as a reductant because the energies of their valence orbitals increase rapidly under pressure and become significantly higher than those of the valence orbitals of oxidant elements. For example, DFT/GA simulations showed that XeO, XeO₂, and XeO₃ become stable at pressures above 83, 102, and 114 GPa.²⁶ A study that combined DAC experiment and DFT simulation work added two new compositions, Xe₃O₂ and Xe₂O₅, in which Xe adopt mixed oxidation states.²⁷ Similarly, Kr-O,²⁸ Xe-N,²⁹ and Xe-C³⁰ compounds are

predicted by DFT/GA, DFT/PSO and DFT/GA methods respectively. Probably, the most striking prediction is the formation of stable Xe-Fe and Xe-Ni compounds under high pressure,³¹ which has been confirmed by DAC experiments.^{32,33} Especially, the DFT/PSO calculations showed that XeFe₃ and XeNi₃ become stable at the pressures and temperatures found in the Earth's core, indicating that the iron core of the Earth might be a chemical reservoir of the missing Xe.³¹ From the chemistry point of view, it is significant that Xe can be oxidized by Fe or Ni under high pressure, as shown by the large calculated charge transfer from Xe to Fe/Ni in these compounds. The alloying of Xe with transition metals such as Hg has been predicted before, but DFT calculations showed only slight charge transfer from Xe to Hg.⁴

2.2 Anionic noble gases under pressure

Besides extending the range of reductant chemistry, pressure can endow a new role for NG elements. They might oxidize metals such as Li and Mg and become anions in the corresponding compounds.^{34–36} The first example was predicted by DFT/PSO method, which showed that Mg forms stable compounds with Xe, Kr, and Ar under pressures higher than 125, 250 and 250 GPa, respectively.³⁴ Among all the calculated compositions, MgNG and Mg₂NG are stable under high pressure. These compounds adopt very simple structures. For Xe and Kr, MgNG adopts $Pm\bar{3}m$ (CsCl) structure, whereas Mg₂NG adopts a P₄/nmm structure. In contrast, both MgAr and Mg₂Ar compounds adopt hexagonal P6₃/mcm structures. The most important chemical feature of these compounds is the charge transfer. As calculated by Bader's Quantum Theory of Atoms in Molecules method,³⁷ there are large charges transferred from Mg to NG, which also strongly depend on the pressure.³⁴ For example, the charge transfer from Mg to Xe in MgXe under 100 GPa is 1.5e/Mg, which is comparable to that in MgO at ambient condition. From the band structures, these compounds are clearly metallic. The projected density of states (PDOS) reveals that the transferred electrons occupy the Xe 5d orbitals.³⁴ Therefore, under high pressure, Xe behaves like a 5d transition metal. The electron localization function (ELF)³⁸ calculations also show large values between Mg and NG, which is also the characteristic of intermetallic compounds. Similar phenomenon has not been found or predicted in any case without compression. The closest sign of anionic NG is a theoretical study that shows a positive electron affinity for Oganesson,³⁹ a synthetic element that has a half-life of about 1ms.



Figure 1. Electronic structure and geometry of compounds containing anionic noble gases and NG-NG covalent bonds. a. Electron localization function (ELF) of Mg₂Kr at 200 GPa; **b.** ELF of Mg₂Ar at 200 GPa; **c.** Structure of Xe₂F at 200 GPa; **d.** The view of one set of Xe atoms in a graphene-like lattice in Xe₂F. The bond lengths are slightly different due to the distortion. **e.** The low pressure (S_L) and the high pressure (S_H) structures of XeO₃ and the O path for the transition from S_L to S_H or vice versa.

The Mg-rich compounds show another unique feature in their electronic structures. The charges on Mg and NG do not add up to 0. For example, at 50 GPa, the charges on Xe and Mg are -1.03e/Xe and 1.29e/Mg. There are about 1.54e do not locate on either Mg or Xe.³⁴ Both the charge distribution and the ELF plots show that these charges locate at the interstitial sites between Mg and NG atoms (Figs. 1a and 1b). Therefore, Mg₂NG is a high-pressure electride (HPE). Electrides are compounds in which some electrons detach from all the atoms and locate at the interstitial sites, playing the role of anions.⁴⁰ The formation of electrides under high pressure can be explained by the energy change of a local orbital constrained at an interstitial site by the surrounding atoms.⁴¹ Although its energy increases due to the reduced volume under increasing pressure, it may changes less significantly than the energies of many atomic orbitals. A series of calculations of these orbital energy changes using a He-matrix model showed that the local orbital energy of the interstitial quasi-atoms (ISQ) decreases relative to that of s and p orbitals with a rate that strongly depends on the atom and the orbital.⁴¹ HPE can form while the energy of ISQ becomes

significantly lower than the energy of valence orbitals of the atom, for example, Li and Na. Mg metal has been predicted to become an HPE under pressures higher than 800 GPa.⁴² The insertion of NG atoms into the Mg lattice while forming Mg-Xe compounds significantly lowers the pressure of forming HPE.

2.3 NG-NG covalent bonds in simple compounds

The examples of chemical bonds between NG atoms are rare. In principle, they do not form bonds because their valence orbitals are completely filled. However, while one or both NG atoms lose electrons, they may form bonds. Examples of this kind include the Xe-Xe bonds in molecules HXeXeR and RXeXeR' (R,R'=F, Cl, Br, I)⁴³, and the Xe²⁺ cations occurs in Xe₂+(Sb₄ F_{21})^{-.44} More recently, an example of the Xe-Xe bond was found unexpectedly in novel Xe-F compounds under pressure.⁴⁵ An experimental study of XeF₂ under compression showed that the XeF₂ molecular crystal transformed into 2D and 3D extended solids and become metallic.⁴⁶ However, the later DFT study did not agree with the proposed structure evolution of XeF₂ under pressure, and therefore cannot explain the observed metallization of the compound.⁴⁷ This discrepancy was alleviated by a full-scale computation study of the Xe-F compounds with various compositions.⁴⁵ The PSO based structure search revealed that XeF₂ becomes unstable and decomposes to Xe₂F and XeF₄ at 81 GPa.⁴⁵ DFT calculations using HSE functional show that XeF₂ maintains its energy gap at least up to 100 GPa, whereas Xe₂F is metallic. The observed insulator-metal transition of XeF_2 at 70 GPa might be caused by the partial decomposition of the sample. The metallic transition was not observed in a later experiment where pressure is applied up to 80 GPa without heating the sample.⁴⁸ Throughout its stable pressure range (60 – 200 GPa), Xe₂F adopts an I4/mcm structure (Fig. 1c) consisting of intercalated Xe graphitic (graphene-like) layers (Fig. 1d).⁴⁵ At 200 GPa, the Xe-Xe distances are 2.573 and 2.636 Å (Fig. 1d), which is close to the summation of the covalent radius of two Xe atoms. The calculated COHP and ELF prove that the two neighboring Xe atoms form covalent bonds.⁴⁵ The appearance of Xe-Xe bonds in a simple binary compound is due to the enhancement of homonuclear bond strength under pressure.¹⁹ It causes the instability of XeF₂, a stoichiometric compound consisting of Xe in its typical oxidation state of +2.

2.4 Noble gas bonds

Another type of chemical interaction that has been missing in noble gas chemistry is the donor-acceptor weak interaction between molecules, which is similar to hydrogen bonds.⁴⁹ Although this type of bond is the strongest for hydrogen, especially while H atoms are bonded with strong oxidant elements such as F and O and become very electrophilic, it has been found for other elements. It was extended to halogens where they are named halogen bonds,⁵⁰ and then to chalcogens, pnictogens, etc.⁵⁰ Up till recently, almost all groups of elements in the periodic table have been found to form this type of bonds, except noble gases. Recently, Frontera et al. studied the molecular electrostatic potential surface of XeO₃ and showed that there was an unexpectedly positive potential at the position of the lone pair of Xe⁶⁺,⁵¹

indicating Xe are very electrophilic while in high oxidation state and can form a noble gas bond. Similar bonding features are also found in XeO₃ and alkylnitrile adducts.²⁵

Under increasing pressure, molecular crystals bound by hydrogen bonds behave very differently to molecular crystals without it. In the latter case, the lengths of the covalent intramolecular bonds, such as C-H bonds in CH₄, decrease while the intermolecular distances are reduced by pressure. In contrast, the lengths of some intramolecular bonds, such as H-O in H₂O, increases under compression, if the hydrogen bonds dominate the intermolecular interactions. In accordance with this change, some vibration modes are softened by the external pressure, opposing our chemical intuition that all vibration frequencies should increase while the material is compressed. Therefore, the change of bond lengths and vibration modes under pressure can be used to demonstrate the presence of hydrogen bonds. The same idea can be applied to noble gas bonds. As shown by a recent computational work of Hou et. al., under increasing pressure, the Xe-O bond lengths of both S_L and S_H increase, and the vibration frequencies of S_H decrease.⁵² Furthermore, the strong noble gas bonds between XeO₃ molecules under pressure might provide transition paths for O atoms from one Xe to a neighboring Xe, a process that is essential for the structural transitions between S_L and S_H (Fig. 1e).⁵³

2.5 Forming compounds while keeping nobility

Being the second abundant element in the universe, Helium has the highest ionization energy of 24.59 eV and a negative electron affinity. Thus, He shows much less chemistry than most other elements in the periodic table. Yet, several chemical species have been predicted or synthesized by locking He in an unusual chemical environment by exquisitely designed molecular scaffolding.^{7–9,54,55} In contrast, the chemistry of He in solid compounds is almost a blank slate except the insertion of He into solid compounds with clathrate or cage structures.^{10,11} Up till very recently, there is no known reaction of He that can form stable solid compound. The first example of such kind is proposed by a thorough structure search study of elements in the periodic table reacting with He under pressure and confirmed by DAC experiment. Most of the elements were found not to react with He except Na that will form stable Na₂He compound under pressure higher than 113 GPa.⁵⁶ The enthalpy of formation is as large as 0.35 eV/atom at a pressure of 350 GPa. Such a large energy gain during the reaction excluded the possibility that Na₂He is bound by weak interactions such as vdW. On the other hand, electronic structure analysis did not show any evidence that He form chemical bonds with neighboring Na atoms, which immediately give rise to a question: how can He form a stable compound without forming chemical bonds?⁵⁷

The answer to this paradox lies in the unusual behavior of electrons in Na under pressure. At pressures higher than 200 GPa, Na undergoes a structural transition and becomes transparent due to the presence of a large band-gap.⁵⁸ In this double-hexagonal closed-packed structure, the valence electrons of Na detach from all the Na atoms and locate at the interstitial sites and play the role of anions. Electron analysis showed that Na₂He is also an HPE,⁵⁶ although Na atoms form a simple cubic

lattice in Na₂He. Therefore the reaction can be viewed as the insertion of He into Na₂E ionic compound. Indeed, soon after the discovery of Na₂He, the reaction of He with several other ionic compounds such as Na₂O,⁵⁶ Na₂S,⁵⁹ H₂O,⁶⁰ etc. have been predicted by DFT calculations. Similar to Na₂He, He does not form chemical bonds with neighboring atoms in these compounds.



Figure 2. Mechanism of He insertion reaction with ionic compounds. a. The schematics of He insertions into AB and AB₂ types of ionic compounds. The Madelung energy increases in the former case whereas decreases in the latter case; **b.** The rocksalt structure of MgO under high pressure; **c.** The lowest energy structure of conceived compound MgOHe; **d.** The view from (001) direction of MgOHe structure, showing that He chains are inserted between Mg and O atoms; **e.** The PbCl₂ structure of MgF₂ under pressure; **f.** The structure of stable MgF₂He compound; **g.** The (110) plane of MgF₂He structure. The He atoms are inserted in between the neighboring F atoms, which further demonstrated the proposed mechanism.

The driving force of He insertion reactions is electrostatic.^{61,62} The key point is that all the above ionic compounds involved in He insertion possess unequal numbers of cations

and anions, although the overall charge is neutral. The mechanism can be explained more easily by a one-dimensional model (Fig. 2a).⁶¹ While reacting with AB type of ionic compounds, He needs to be inserted in between two ions with opposite charges and therefore increase the electrostatic (Madelung) energy. In contrast, if the ionic compound is A_2B (or AB_2) type, He atoms can choose to stay in between two ions (such as A^+) with the same charge and therefore lower the Madelung energy. The two A^+ ions repel each other, but are forced to stay close by external pressure. The insertion of the He in between two A^+ ions alleviates this pressure effect, therefore the insertion of He in this type of ionic compounds becomes favored under increasing pressure. Thus, the reaction does not involve the formation of any local chemical bond, i.e. He can react with ionic compounds while keeping its chemical inertness (nobility). This mechanism has been demonstrated by rigorous energy analysis for He insertion into MgO (AB type) and MgF₂ (AB₂ type) compounds (Fig. 2b-2g).⁶¹

Conclusions and perspectives

Many recent simulations and experiments showed that noble gases could have very rich chemistry under high pressure. The types of chemical roles and interactions include electron donors (being oxidizing), electron acceptors (being reduced), NG-NG covalent bonds, noble gas bonds, and reliever of repulsive electrostatic interactions. A major effect of pressure is the change of the energies of the atomic orbitals. Although the energies of all local orbitals increase under higher pressure, those with higher because the electrons are more confined in the compressed solid. However, the energies of orbitals with lower principal quantum numbers and sephigher angular momenta, especially those having no corresponding core orbitals such as 2p and 3d, increase less significant when compared with the energies of orbitals with higher principal sepquantum numbers or lower angular momenta. As a result of this orbital energy reordering, the sepelectrons are redistributed in different quantum orbitals under pressure. If the energy of the valence np orbital of a noble gas (5p for Xe, 4p for Kr) is close to or higher than the energies of the valence orbitals of an oxidant element such as F, O, or Fe, the noble gas will be oxidized. Conversely, if the unoccupied orbitals of the noble gases such as 5d for Xe become lower in energy than the orbitals of reductants such as Li or Mg, the noble gases will be reduced and become anionic.

The future of the exotic chemistry of noble gases as well as the high-pressure study rely on three signs of progress, the experimental methods that allow us to study the chemistry of materials under higher pressure (>200 GPa), the computer power and the simulation algorithms that can enable us to explore the structures and stability of more complicated materials such as ternary and quaternary compounds, the conceptual framework that can help us understanding and predicting the change of chemistry under pressure without fullscale calculations. Although the recent high-pressure studies have greatly advanced the noble gas chemistry, many important questions still remain unanswered. What are the oxidation and reduction limits of noble gases? Can He or Ne be oxidized or reduced under pressure? Can high-pressure noble gas compounds become superconducting or topological? Can high-pressure noble gas bonding be recovered after releasing the pressure? The developments of theoretical, simulation, and experimental methods might help to answer these questions and extend the noble gas chemistry to an unexpected territory.

Acknowledgments The author acknowledges the support of the National Science Foundation under Grant No. DMR-1848141, the ACS PRF under Grant No. 59249-UNI6, and computational resources provided by XSEDE (TG-DMR130005).

References

- (1) Pauling, L. The Formulas of Antimonic Acid and the Antimonates. J. Am. Chem. Soc. **1933**, 55 (5), 1895–1900. https://doi.org/10.1021/ja01332a016.
- (2) Bartlett, N. Xenon Hexafluoroplatinate (V) Xe⁺PtF₆. *Proceedings of the Chemical Society of London* **1962**, No. JUN.
- Chernick, C. L.; Claassen, H. H.; Fields, P. R.; Hyman, H. H.; Malm, J. G.; Manning, W. M.; Matheson, M. S.; Quarterman, L. A.; Schreiner, F.; Selig, H. H.; Sheft, I.; Siegel, S.; Sloth, E. N.; Stein, L.; Studier, M. H.; Weeks, J. L.; Zirin, M. H. Fluorine Compounds of Xenon and Radon. *Science* 1962, *138* (3537), 136–138. https://doi.org/10.1126/science.138.3537.136.
- (4) Grochala, W. Atypical Compounds of Gases, Which Have Been Called "Noble." *Chem. Soc. Rev.* **2007**, *36* (10), 1632–1655. https://doi.org/10.1039/b702109g.
- (5) Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Rasanen, M. A Stable Argon Compound. *Nature* **2000**, *406* (6798), 874–876.
- Seidel, S.; Seppelt, K. Xenon as a Complex Ligand: The Tetra Xenono Gold(II) Cation in AuXe42+(Sb2F11-)2. *Science* 2000, 290 (5489), 117–118. https://doi.org/10.1126/science.290.5489.117.
- (7) Hogness, T. R.; Lunn, E. G. The Ionization of Hydrogen by Electron Impact as Interpreted by Positive Ray Analysis. *Phys. Rev.* 1925, 26 (1), 44–55. https://doi.org/10.1103/PhysRev.26.44.
- (8) Li, T. H.; Mou, C. H.; Chen, H. R.; Hu, W. P. Theoretical Prediction of Noble Gas Containing Anions FNgO- (Ng = He, Ar, and Kr). J. Am. Chem. Soc. 2005, 127 (25), 9241–9245. https://doi.org/10.1021/ja051276f.
- (9) Grochala, W. A Metastable He-O Bond inside a Ferroelectric Molecular Cavity: (HeO)(LiF)(2). *Phys. Chem. Chem. Phys.* 2012, *14* (43), 14860–14868. https://doi.org/10.1039/c2cp42321a.
- (10) Saunders, M.; Jimenez-Vazquez, H. A.; Cross, R. J.; Mroczkowski, S.; Gross, M. L.; Giblin, D. E.; Poreda, R. J. Incorporation of Helium, Neon, Argon, Krypton, and Xenon into Fullerenes Using High Pressure. J. Am. Chem. Soc. 1994, 116 (5), 2193–2194. https://doi.org/10.1021/ja00084a089.
- (11) Guńka, P. A.; Dziubek, K. F.; Gładysiak, A.; Dranka, M.; Piechota, J.; Hanfland, M.; Katrusiak, A.; Zachara, J. Compressed Arsenolite As4O6 and Its Helium Clathrate As4O6·2He. *Crystal Growth & Design* 2015, *15* (8), 3740–3745. https://doi.org/10.1021/acs.cgd.5b00390.
- (12) Zhang, L.; Wang, Y.; Lv, J.; Ma, Y. Materials Discovery at High Pressures. *Nature Reviews Materials* **2017**, *2* (4). https://doi.org/10.1038/natrevmats.2017.5.
- (13) Oganov, A. R.; Pickard, C. J.; Zhu, Q.; Needs, R. J. Structure Prediction Drives Materials Discovery. *Nature Reviews Materials* 2019, 4 (5), 331–348. https://doi.org/10.1038/s41578-019-0101-8.

- (14) Mao, H. K.; Chen, X. J.; Ding, Y.; Li, B.; Wang, L. Solids, Liquids, and Gases under High Pressure. *Rev. Mod. Phys.* **2018**, *90* (1). https://doi.org/ARTN 015007 10.1103/RevModPhys.90.015007.
- (15) Zhang, W.; Oganov, A. R.; Goncharov, A. F.; Zhu, Q.; Boulfelfel, S. E.; Lyakhov, A. O.; Somayazulu, M.; Prakapenka, V. B. Unexpected Stable Stoichiometries of Sodium Chlorides. 2012, arXiv:1211.3644.
- (16) Drozdov, A. P.; Eremets, M. I.; Troyan, I. A.; Ksenofontov, V.; Shylin, S. I. Conventional Superconductivity at 203 Kelvin at High Pressures in the Sulfur Hydride System. *Nature* 2015, *525* (7567), 73–76. https://doi.org/10.1038/nature14964.
- (17) Pickard, C. J.; Errea, I.; Eremets, M. I. Superconducting Hydrides Under Pressure. Annual Review of Condensed Matter Physics 2020, 11 (1), 57–76. https://doi.org/10.1146/annurev-conmatphys-031218-013413.
- (18) Miao, M. S. Caesium in High Oxidation States and as a P-Block Element. *Nat Chem* **2013**, *5* (10), 846–852. https://doi.org/10.1038/nchem.1754.
- (19) Miao, M.; Sun, Y.; Zurek, E.; Haiqing, L. Chemistry under High Pressure. *Nature Review Chemistry* **2020**, *to appear*.
- (20) Pickard, C. J.; Needs, R. J. Ab Initio Random Structure Searching. *J Phys Condens Matter* **2011**, *23* (5), 053201. https://doi.org/10.1088/0953-8984/23/5/053201.
- (21) Glass, C. W.; Oganov, A. R.; Hansen, N. USPEX Evolutionary Crystal Structure Prediction. *Comput. Phys. Commun.* 2006, 175 (11–12), 713–720. https://doi.org/10.1016/j.cpc.2006.07.020.
- (22) Avery, P.; Toher, C.; Curtarolo, S.; Zurek, E. XtalOpt Version R12: An Open-Source Evolutionary Algorithm for Crystal Structure Prediction. *Computer Physics Communications* **2019**, *237*, 274–275. https://doi.org/10.1016/j.cpc.2018.11.016.
- (23) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. CALYPSO: A Method for Crystal Structure Prediction. *Comput. Phys. Commun.* **2012**, *183* (10), 2063–2070. https://doi.org/10.1016/j.cpc.2012.05.008.
- (24) Brock, D. S.; Schrobilgen, G. J. Synthesis of the Missing Oxide of Xenon, XeO2, and Its Implications for Earth's Missing Xenon. J. Am. Chem. Soc. 2011, 133 (16), 6265–6269. https://doi.org/10.1021/ja110618g.
- (25) Goettel, J. T.; Matsumoto, K.; Mercier, H. P. A.; Schrobilgen, G. J. Syntheses and Structures of Xenon Trioxide Alkylnitrile Adducts. *Angewandte Chemie International Edition* 2016, 55 (44), 13780–13783. https://doi.org/10.1002/anie.201607583.
- (26) Zhu, Q.; Jung, D. Y.; Oganov, A. R.; Glass, C. W.; Gatti, C.; Lyakhov, A. O. Stability of Xenon Oxides at High Pressures. *Nat Chem* 2013, 5 (1), 61–65. https://doi.org/10.1038/nchem.1497.
- (27) Dewaele, A.; Worth, N.; Pickard, C. J.; Needs, R. J.; Pascarelli, S.; Mathon, O.; Mezouar, M.; Irifune, T. Synthesis and Stability of Xenon Oxides Xe2O5 and Xe3O2 under Pressure. *Nat Chem* 2016, 8 (8), 784–790. https://doi.org/10.1038/nchem.2528.
- (28) Zaleski-Ejgierd, P.; Lata, P. M. Krypton Oxides under Pressure. Scientific reports 2016, 6, 18938. https://doi.org/10.1038/srep18938.

- (29) Peng, F.; Wang, Y. C.; Wang, H.; Zhang, Y. W.; Ma, Y. M. Stable Xenon Nitride at High Pressures. *Phys. Rev. B* 2015, *92* (9). https://doi.org/10.1103/PhysRevB.92.094104.
- (30) Bovornratanaraks, T.; Tsuppayakorn-aek, P.; Luo, W.; Ahuja, R. Ground–State Structure of Semiconducting and Superconducting Phases in Xenon Carbides at High Pressure. *Scientific Reports* 2019, 9 (1), 1–6. https://doi.org/10.1038/s41598-019-39176-4.
- (31) Zhu, L.; Liu, H.; Pickard, C. J.; Zou, G.; Ma, Y. Reactions of Xenon with Iron and Nickel Are Predicted in the Earth's Inner Core. *Nat Chem* **2014**, *6* (7), 644–648. https://doi.org/10.1038/nchem.1925.
- (32) Dewaele, A.; Pépin, C. M.; Geneste, G.; Garbarino, G. Reaction between Nickel or Iron and Xenon under High Pressure. *High Pressure Research* 2017, *37* (2), 137– 146. https://doi.org/10.1080/08957959.2016.1267165.
- (33) Stavrou, E.; Yao, Y.; Goncharov, A. F.; Lobanov, S. S.; Zaug, J. M.; Liu, H.; Greenberg, E.; Prakapenka, V. B. Synthesis of Xenon and Iron-Nickel Intermetallic Compounds at Earth's Core Thermodynamic Conditions. *Phys. Rev. Lett.* 2018, *120* (9), 096001. https://doi.org/10.1103/PhysRevLett.120.096001.
- (34) Miao, M. S.; Wang, X. L.; Brgoch, J.; Spera, F.; Jackson, M. G.; Kresse, G.; Lin, H. Q. Anionic Chemistry of Noble Gases: Formation of Mg-NG (NG = Xe, Kr, Ar) Compounds under Pressure. J. Am. Chem. Soc. 2015, 137 (44), 14122–14128. https://doi.org/10.1021/jacs.5b08162.
- (35) Li, X.; Hermann, A.; Peng, F.; Lv, J.; Wang, Y.; Wang, H.; Ma, Y. Stable Lithium Argon Compounds under High Pressure. *Scientific reports* **2015**, *5*, 16675. https://doi.org/10.1038/srep16675.
- (36) Liu, Z.; Botana, J.; Miao, M. S.; Yan, D. D. Unexpected Xe Anions in XeLin Intermetallic Compounds. *Epl* 2017, *117* (2). https://doi.org/10.1209/0295-5075/117/26002.
- (37) Bader, R. Atoms in Molecules: A Quantum Theory; Oxford University Press, 1990.
- (38) Silvi, B.; Savin, A. Classification of Chemical Bonds Based on Topological Analysis of Electron Localization Functions. *Nature* **1994**, *371* (6499), 683–686. https://doi.org/10.1038/371683a0.
- (39) Gaston, N.; Schwerdtfeger, P.; Nazarewicz, W. Ionization Potentials of Internal Conversion Electrons for the Superheavy Elements 112, 114, 116, and 118. *Phys. Rev. A* 2002, 66 (6), 062505. https://doi.org/10.1103/PhysRevA.66.062505.
- (40) Dawes, S. B.; Ward, D. L.; Huang, R. H.; Dye, J. L. First Electride Crystal Structure. J. Am. Chem. Soc. 1986, 108 (12), 3534–3535. https://doi.org/10.1021/ja00272a073.
- (41) Miao, M.-S.; Hoffmann, R. High Pressure Electrides: A Predictive Chemical and Physical Theory. *Acc. Chem. Res.* **2014**, *47* (4), 1311–1317. https://doi.org/10.1021/ar4002922.
- (42) Li, P.; Gao, G.; Wang, Y.; Ma, Y. Crystal Structures and Exotic Behavior of Magnesium under Pressure. J. Phys. Chem. C 2010, 114 (49), 21745–21749. https://doi.org/10.1021/jp108136r.
- (43) Fernández, I.; Frenking, G. Neutral Noble Gas Compounds Exhibiting a Xe–Xe Bond: Structure, Stability and Bonding Situation. *Phys. Chem. Chem. Phys.* 2012, 14 (43), 14869–14877. https://doi.org/10.1039/C2CP41244F.

- (44) Drews, T.; Seppelt, K. The Xe Ion—Preparation and Structure. *Angewandte Chemie International Edition in English* **1997**, *36* (3), 273–274. https://doi.org/10.1002/anie.199702731.
- (45) Peng, F.; Botana, J.; Wang, Y.; Ma, Y.; Miao, M. Unexpected Trend in Stability of Xe-F Compounds under Pressure Driven by Xe-Xe Covalent Bonds. *The journal of physical chemistry letters* 2016, 7 (22), 4562–4567. https://doi.org/10.1021/acs.jpclett.6b01922.
- (46) Kim, M.; Debessai, M.; Yoo, C. S. Two- and Three-Dimensional Extended Solids and Metallization of Compressed XeF2. *Nat Chem* 2010, 2 (9), 784–788. https://doi.org/10.1038/nchem.724.
- (47) Kurzydlowski, D.; Zaleski-Ejgierd, P.; Grochala, W.; Hoffmann, R. Freezing in Resonance Structures for Better Packing: XeF2 Becomes (XeF+)(F-) at Large Compression. *Inorg. Chem.* 2011, 50 (8), 3832–3840. https://doi.org/10.1021/ic200371a.
- (48) Wu, G.; Huang, X.; Huang, Y.; Pan, L.; Li, F.; Li, X.; Liu, M.; Liu, B.; Cui, T. Confirmation of the Structural Phase Transitions in XeF2 under High Pressure. J. Phys. Chem. C 2017, 121 (11), 6264–6271. https://doi.org/10.1021/acs.jpcc.6b11558.
- (49) Pauling, L. The Nature of the Chemical Bond; Cornell Uni- versity Press, 1960.
- (50) Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. The Halogen Bond. *Chem. Rev.* 2016, *116* (4), 2478–2601. https://doi.org/10.1021/acs.chemrev.5b00484.
- (51) Bauzá, A.; Frontera, A. Aerogen Bonding Interaction: A New Supramolecular Force? *Angewandte Chemie International Edition* **2015**, *54* (25), 7340–7343. https://doi.org/10.1002/anie.201502571.
- (52) Hou, C.; Wang, X.; Botana, J.; Miao, M. Noble Gas Bond and the Behaviour of XeO3 under Pressure. *Phys. Chem. Chem. Phys.* 2017, 19 (40), 27463–27467. https://doi.org/10.1039/c7cp05385a.
- (53) Hou, P.; Tian, F.; Li, D.; Zhao, Z.; Duan, D.; Zhang, H.; Sha, X.; Liu, B.; Cui, T. Ab Initio Study of Germanium-Hydride Compounds under High Pressure. *RSC Advances* 2015, 5 (25), 19432–19438. https://doi.org/10.1039/c4ra13183e.
- (54) Hotokka, M.; Kindstedt, T.; Pyykkö, P.; Roos, B. O. On Bonding in Transition-Metal Helide Ions. *Molecular Physics* 1984, 52 (1), 23–32. https://doi.org/10.1080/00268978400101031.
- (55) Rzepa, H. S. The Rational Design of Helium Bonds. *Nature Chemistry* **2010**, *2* (5), 390–393. https://doi.org/10.1038/nchem.596.
- (56) Dong, X.; Oganov, A. R.; Goncharov, A. F.; Stavrou, E.; Lobanov, S.; Saleh, G.; Qian, G. R.; Zhu, Q.; Gatti, C.; Deringer, V. L.; Dronskowski, R.; Zhou, X. F.; Prakapenka, V. B.; Konopkova, Z.; Popov, I. A.; Boldyrev, A. I.; Wang, H. T. A Stable Compound of Helium and Sodium at High Pressure. *Nat Chem* 2017, 9 (5), 440–445. https://doi.org/10.1038/nchem.2716.
- (57) Miao, M. Helium Chemistry: React with Nobility. *Nat Chem* **2017**, *9* (5), 409–410. https://doi.org/10.1038/nchem.2768.
- Ma, Y.; Eremets, M.; Oganov, A. R.; Xie, Y.; Trojan, I.; Medvedev, S.; Lyakhov, A. O.; Valle, M.; Prakapenka, V. Transparent Dense Sodium. *Nature* 2009, 458 (7235), 182–185. https://doi.org/10.1038/nature07786.

- (59) Gao, H.; Sun, J.; Pickard, C. J.; Needs, R. J. Prediction of Pressure-Induced Stabilization of Noble-Gas-Atom Compounds with Alkali Oxides and Alkali Sulfides. *Physical Review Materials* 2019, 3 (1), 015002. https://doi.org/10.1103/PhysRevMaterials.3.015002.
- (60) Liu, H. Y.; Yao, Y. S.; Klug, D. D. Stable Structures of He and H2O at High Pressure. *Phys. Rev. B* 2015, *91* (1). https://doi.org/10.1103/PhysRevB.91.014102.
- (61) Liu, Z.; Botana, J.; Hermann, A.; Valdez, S.; Zurek, E.; Yan, D.; Lin, H. Q.; Miao, M. S. Reactivity of He with Ionic Compounds under High Pressure. *Nature communications* 2018, 9 (1), 951. https://doi.org/10.1038/s41467-018-03284-y.
- (62) Bai, Y.; Liu, Z.; Botana, J.; Yan, D.; Lin, H.-Q.; Sun, J.; Pickard, C. J.; Needs, R. J.; Miao, M.-S. Electrostatic Force Driven Helium Insertion into Ammonia and Water Crystals under Pressure. *Commun Chem* 2019, *2* (1), 1–7. https://doi.org/10.1038/s42004-019-0204-6.