Forcing Cesium into Higher Oxidation States Using Useful hard x-ray Induced Chemistry under High Pressure

D Sneed¹, M Pravica¹, E Kim¹, N Chen³, C Park², M White¹
¹ Department of Physics and Astronomy, and High Pressure Science and Engineering Center, University of Nevada Las Vegas, 4505 Maryland Parkway, Las Vegas, NV
² HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, 9700 South Cass Ave., 434E, Argonne, IL, 60439, USA
³ Canadian Light Source Inc., 44 Innovation Boulevard, Saskatoon, SK S7N 2V3, Canada

Daniel Sneed: sneedd3@unlv.nevada.edu, Michael Pravica: pravica@physics.unlv.edu

Abstract. This paper discusses our attempt to synthesize higher oxidation forms of cesium fluoride by pressurizing cesium fluoride in a fluorine-rich environment created via the x-ray decomposition of potassium tetrafluoroborate. This was done in order to confirm recent theoretical predictions of higher oxidation forms of CsFₙ. We discuss the development of a technique to produce molecular fluorine in situ via useful hard x-ray photochemistry, and the attempt to utilize this technique to form higher oxidation states of cesium fluoride. In order to verify the formation of the novel stoichiometric species of CsFₙ, X-ray Absorption Near Edge Spectroscopy (XANES) centered on the cesium K-edge was performed to probe the oxidation state of cesium as well as the local molecular coordination around Cs.

1. Introduction

Recent theoretical work has predicted that cesium may undergo inner-shell (p-shell) bonding with fluorine under high pressure, forming higher oxidation species CsFₙ (n=2-6) [1]. Though inner shell electrons are normally inaccessible for bonding under ambient conditions, pressure can broaden and increase the energy of the 5p shell of cesium, allowing the electrons to interact with a highly oxidizing atom such as fluorine. Thus, though cesium has only one valence electron in the 6s shell to contribute to bonding (giving it a formal oxidation state of 1+), it has been predicted that the highly electronegative fluorine will begin to pull electrons out of the 5p shell causing cesium and fluorine to undergo xenon like bonding under pressures greater than 10 GPa[1].

The primary difficulty in synthesizing new CsFₙ compounds is that fluorine is difficult to work due to its extremely reactive nature caused by its high electronegativity. Recent developments in useful hard x-ray induced chemistry [2-7] offer a method to produce simple molecules for reaction in situ within a diamond anvil cell by decomposing relatively safe, inert, easy-to-handle solid crystalline powders using the highly ionizing and highly penetrating characteristics of hard x-rays (>7keV). Using this technique, multiple species of simple molecules have been formed, including H₂, N₂, O₂, Cl₂, and most recently F₂, all in situ within a diamond anvil cell [2-7]. It has also been shown that highly controlled chemistry can be achieved at high pressures via the reaction to produce molecular hydrogen (formed by the x-ray induced decomposition of ammonia borane) and molecular oxygen (formed by the x-ray induced decomposition of potassium perchlorate), which then react to form water; all in situ within a diamond anvil cell at high pressure [5]. OF₂ has also been formed by similar methods [7]. This experiment, combined with the successful formation of molecular fluorine via useful hard x-ray induced chemistry has given us a novel means to release F₂ and perform fluorine chemistry under extreme conditions all in situ.
Here we report on experiments that attempt to combine the recent developments of useful x-ray induced chemistry with the theoretical prediction presented by Miao [1] in order to synthesize these higher oxidation states of CsFₙ under high pressures. Through the use of Raman spectroscopy to verify the production of molecular fluorine, and cesium K-edge XANES to probe the valence state of cesium as well as local atomic coordination around the cesium atom, we demonstrate the synthesis of these novel CsFₙ stoichiometric species via useful hard x-ray induced chemistry confined within a diamond anvil cell.

2. Experiment

It has been previously demonstrated that the formation of F₂ can be achieved via the x-ray decomposition of C₆F₁₄ [4] and potassium tetrafluoroborate [7], verifying that both compounds could be used as sources for molecular fluorine using useful x-ray induced chemistry. The production of molecular fluorine was verified via Raman spectroscopy [4, 7]. We chose to use powdered KBF₄ for ease of mixing with CsF.

![Figure 1: Raman spectra of segregated mixture of ammonia borane and potassium perchlorate showing the H₂O vibrational modes post x-ray irradiation at 5 GPa [fig. 2 of reference 5]](image1)

![Figure 2: (left) Raman spectra of unirradiated KBF₄, (right) Raman spectra of irradiated KBF₄ showing the fluorine vibron at ∼903 cm⁻¹ [fig. 2 of reference 7]](image2)
The first stage of our experiment consisted of a high pressure X-ray Absorption Near Edge Spectroscopy (XANES) experiment. A panoramic-style diamond anvil cell with a Be gasket pre-indented to 50 μm thickness and subsequently laser-drilled to make a 120 μm hole forming the sample chamber. The hole was loaded with a 1:1 ratio by mass mixture of KBF₄ (Sigma-Aldrich 99%) and CsF (Sigma-Aldrich 99%) under argon. A small 20 μm, thermally-relieved ruby sphere was placed in with the sample for pressure measurements. The cell was sealed and pressurized to ~3 GPa in order to seal the mixture and then irradiated at the 16 BM-B beamline of the Advanced Photon Source of Argonne National Laboratory. “White” x-ray radiation in the 10 – 70 KeV energy range was used to decompose the KBF₄ to produce molecular fluorine, which would be available to react with CsF to potentially synthesize the novel CsF₂ stoichiometric species. The sample mixture was placed into the path of an unfocused 80 μm by 80 μm x-ray beam for approximately 8 hours.

The DAC was then pressurized to 16 GPa and placed in the 16 BM-D beamline at the Advanced Photon Source of Argonne National Laboratory. The cell was placed in radial transmission geometry to the beam path so that absorption measurements through the beryllium gasket containing the sample could be made. A focused 8 μm by 8 μm monochromatic x-ray beam centered at the 35.985 keV Cs K-edge was used to probe the sample. All measurements were made in transmission mode. The monochromator was scanned from 400 eV below the edge to 800 eV above the edge. The energy resolution of the monochromator was 8-10 eV. Photon counting was performed pre- and post-sample using a mixture of argon and xenon gas-filled ion chambers for incident and transmitted x-ray intensity measurements. Measurements were conducted at 16, 53, and 79 GPa. Seven scans were performed at the three different pressures for signal averaging the spectra.

The second stage of our experiments consisted of performing a high pressure XANES experiment of pure CsF for comparison purposes. A panoramic-style DAC with a Be gasket was pre-indented to 50 μm thickness and a 120 μm hole was laser drilled and then loaded with CsF (Sigma-Aldrich 99%) under argon. A small 20 μm, thermally-relieved ruby sphere was placed in with the sample for pressure measurements. The cell was pressurized to 2.7 GPa in order to ensure that the sample was in its low pressure face-centered cubic (fcc) NaCl structure [8]. The experimental geometry and instrumental setup were identical to the first experiment. Measurements were made at 2.7, 12.6, 25, 43, 55, and 78 GPa respectively. Three scans each were performed for each different pressures and signal averaged.

3. Results and discussion

The XANES spectrum of the irradiated mixture displays a demonstrable change in the near edge spectrum of the 79 GPa measurement, which can be seen in the left pane of figure 3; this is indicative of a change to the local molecular structure around the Cs atom. The control measurement of the pure unirradiated CsF did not show the same change to the near edge structure, as shown in the right pane of figure 3, which is to be expected as the body-centered cubic (bcc) CsCl structure of CsF is predicted to be stable up to 200 GPa [1]. CsF undergoes one known structural transition from the low pressure face-centered cubic (fcc) NaCl structure to the high pressure bcc CsCl structure at approximately 4.8 GPa [8], which can be seen to occur in Figure 3 between 2.7 and 12.6 GPa by the down shift in energy of the near edge features at 36025 eV and 36075 eV, which is indicative an increase of the Cs-F bond length, and is to be expected in the transition from the fcc to bcc structure in CsF.
A similar argument can be made for the near edge spectral changes of the irradiated mixture at 79 GPa (left panel of Fig. 3), though the different features of the near edge spectrum change in a much more complicated manner. When comparing the spectrum at 53 GPa to the spectrum at 79 GPa in the left panel of Figure 3, it can be seen that the features at 36030 eV and 36090 eV can be seen to decrease in energy to 36015 eV and 36080 eV respectively, while a new shoulder feature is seen to emerge at 36025 eV. This, along with the changes in relative intensities, suggests that there is far more occurring within the sample that requires further experimentation to verify and properly classify. It should also be noted that visible changes also occurred within the sample chamber of the x-ray photochemistry experiment that did not occur in the pure CsF control experiment. The sample went from being a white semi-translucent color, to dark brown, providing further evidence for a chemical change in the sample.

4. Conclusions

An attempt to synthesize novel stoichiometric species of CsFₙ (n=2-6) was made by pressurizing a mixture of cesium fluoride and KBF₄ that was irradiated in order to create a fluorine-rich atmosphere via useful hard x-ray photochemistry. XANES was utilized to probe potential oxidation state changes of the cesium atom as well as changes in the local molecular structure in order to verify the production of new stoichiometric species of cesium fluoride in higher oxidation states. Our experiments show the
potential formation of a new molecular structure, though further x-ray diffraction and XANES experiments along with theoretical study using the density-functional theory are necessary in order to verify and properly classify these changes. Though we cannot definitively state that we have formed a new species of CsF₆, these experiments provide tantalizing evidence of the possibility that we have formed a new species of CsF₆ and give us strong impetus to investigate this further.

5. Acknowledgments

We thank Yonggang Wang with HPCAT for all of his help with the experiments. We acknowledge support from the Department of Energy National Nuclear Security Administration under Award Number(s) DE-NA0000979, and from the DOE Cooperative Agreement No. DE-FC08-01NV14049 with the University of Nevada, Las Vegas. HPCAT operation is supported by DOE-NNSA under Award No. DE-NA0001974 and DOE-BES under Award No. DE-FG02-99ER45775. HPCAT is supported by DOE-BES, DOE-NNSA, NSF, and the W.M. Keck Foundation. Use of the Advanced Photon Source is supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357

References

[1.] Miao M Caesium high oxidation states and as a p-block element Nature Chem. Vol 5 pp 846-852 (2013) doi: http://dx.doi.org/10.1038/nchem.1754
[2.] Pravica M Popov D Sinogeikin S Sneed D Guardala G Smith Q X-ray induced mobility of molecular oxygen at extreme conditions Applied Phys. Letters (2013) http://dx.doi.org/10.1063/1.4836475
[3.] Pravica M Sneed D Smith Q Bai L High pressure X-ray photochemical studies of carbon tetrachloride: Cl₂ production and segregation Chem. Phys. Letters Volume 590 18 December (2013) pp 74-76 doi: http://dx.doi.org/10.1016/j.cplett.2013.10.056
[4.] Pravica M Sneed D White M Wang Y Note: Loading method of molecular fluorine using x-ray induced chemistry Review of Scientific Instruments, 85, 086110 (2014), doi: http://dx.doi.org/10.1063/1.4893384
[5.] Pravica M Sneed D White M Wang Y Communication: A novel method for generating molecular mixtures at extreme conditions: The case of hydrogen and oxygen J. Chem. Phys. 141 091101 (2014) doi: http://dx.doi.org/10.1063/1.4894402
[6.] Pravica M Liu Y Bai L Hydrazine at High Pressures Chem. Phys. Letters, 555 pp 113-115 (2013) doi: http://dx.doi.org/10.1063/1.4894402
[7.] Pravica M White M Wang Y A novel method for generating molecular mixtures at extreme conditions: The case of fluorine and oxygen Accepted for publication, APS SCCM conference proceedings (2015).
[8.] Merrill Leo Behavior of the AB-type compounds at high pressures and high temperatures Journal of Physical and Chemical Reference Data 6 1205-1252 (1977) doi: http://dx.doi.org/10.1063/1.555569