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Hard x-ray induced synthesis of OF₂

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ABSTRACT

We sought to demonstrate that hard x-rays can initiate a sequence of acatalytic photochemical reactions with the aim of creating molecular mixtures (O₂ and F₂) and then observe the two species react to form OF₂ and with little introduction of heat. Two x-ray Raman scattering (XRS) studies of 1. KBF₄ and 2. a mixture of KBF₄ + KClO₄ pressurized to 3 GPa in a diamond anvil cell (DAC) at ambient temperature at the 16 ID-D undulator beamline at the Advanced Photon Source. The spectrometer collected photons with energy losses around 680 eV near the fluorine K-edge. Fluorine K-edge x-ray Raman spectroscopy demonstrated the clear formation of a new peak near 682 eV energy loss after some 8 hours of irradiation and detection of the KBF₄/KClO₄ mixture which likely represents OF₂ produced from the following reaction: O₂+2F₂→ 2OF₂ following irradiation of the mixture to release O₂ and F₂, respectively, from each constituent.

INTRODUCTION

Fluorine is the most electronegative element, and thus, would be an excellent choice as a reactant to drive novel chemistry under extreme conditions (e.g. inside pressurized diamond anvil cells)(1) for industrial purposes and for fundamental chemical/bonding insights. Understanding how this reactive element interacts with other simple molecular reactants such as O₂ and its mobility under high pressure would be of great interest from the standpoint of better ascertaining the behavior of simple molecular mixtures under shockwave conditions to aid detonation chemistry which occurs at extreme conditions (high pressure and/or high temperature). As there are fluorine-containing explosives (2) which use the NF₂ group as an oxidizing moiety (2, 3) such as 3,3,7,7-tetrakis(difluoramino) octahydro-1,5-dinitro-1,5-diazocine (HNFX)(2) and Bis- and Tris-difluoroamino perfluorobutane (3), and as F₂ can react explosively with some molecules (e.g. H₂), significant insights may also be garnered by the effort of developing fluorine chemistry at extreme conditions.

However, to study fluorine at high pressure, it must be either loaded cryogenically (melting point -219.6°C at 1 atm) or inside a pressure bomb. Both methods possess inherent dangers associated with flowing this toxic and highly reactive gas at either high pressure or low temperature.

As a result, there are few studies of fluorine at high pressure (>1 GPa); in fact, before our efforts to develop fluorine chemistry at high pressure, we were aware of only one study (a Raman spectroscopic study) of molecular fluorine up to 6 GPa (4). Thus, it has been our desire to develop the ability to load fluorine in a very controlled way using highly penetrating (i.e. can be transmitted through diamonds into a pressurized sample), highly ionizing, and highly focused hard x-rays (>7keV, order of micron diameter x-ray beam) that will acatalytically break down selected compounds to release F₂ with the aim of studying fluorine and fluorine-induced chemistry at extreme conditions (1, 5-7). As one example of the utility of this novel fluorine chemistry, Cs and Hg have been predicted to become p-block elements at high pressure and react in the presence of F₂ forming compounds: CsF₂ (7, 8), CsF₃(7, 8) or HgF₄(1) (see Figure 1).

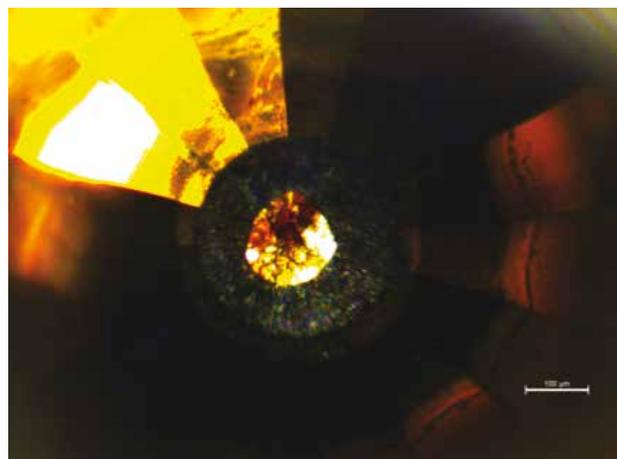


Figure 1. Reddish molecular fluorine which is likely in the a phase pressurized at 70 GPa produced after irradiation of a mixture of CsF and KBF₄ at low pressure (3GPa) and then pressurized up to 70 GPa to create CsF₅(5). Similar to oxygen, solid fluorine changes color with pressure. The photo is taken by looking through one diamond (culets visible) as viewed through a microscope.

Recently, as part of these efforts to observe fluorine reaction chemistry at extreme conditions, we sought to synthesize OF₂ using hard x-rays by irradiating a segregated mixture of KClO₄ and KBF₄ powders which were confined inside a "keyhole"/double hole gasket pressurized by a diamond anvil cell. Irradiation of KClO₄ produced O₂ (via KClO₄ + hv → KCl + 2O₂) and irradiation of KBF₄ produced

F₂. The two products then reacted in the presence of hard x-rays via the following suspected reaction: O₂+2F₂→ 2OF₂ based on Raman spectroscopic evidence (5). From the standpoint of developing fluorine chemistry at extreme or isolated conditions, the ability to produce OF₂ in the solid state via *x-ray induced combustion*⁹ would be of tremendous utility. Also, better understanding how simple and reactive molecular mixtures of O₂ and F₂ diffuse, mix and react under extreme conditions would greatly aid detonation chemistry and contribute data toward modeling codes such as CHEETAH (10).

In that spirit, we sought to confirm that we successfully produced OF₂ via another spectroscopic method: x-ray Raman scattering (XRS). As Raman spectroscopy is sensitive to valence/bonding vibrational states, we sought to use a method that is somewhat less sensitive to high pressure but can unequivocally ascertain any novel bonding/electronic state rearrangement heralding a chemical reaction. Typically this entails accessing deeper electron levels.

In X-ray Raman spectroscopy, core 1s electrons are generally excited by incoming higher energy x-rays into a virtual state which then drops down to a higher energy electronic state (e.g. π→π* transition) wherein the difference between the incoming x-ray and scattered x-rays is near the K-edge of the element in question (11).

Though there are other methods such as x-ray absorption and Electron Energy Loss Spectroscopy (EELS) that can more easily access electronic states, our efforts to develop (and concomitantly understand) fluorine chemistry in the solid state under extreme conditions necessitate performing *in situ* studies inside a sealed/pressurized chamber such as the DAC. This requires using spectroscopic methods that can penetrate the confining gasket and/or diamonds which, in the case of x-rays, are typically greater than 7 keV (12). For our experiments, the incident/gasket-penetrating x-rays are provided by a synchrotron and were above this energy (~10 keV).

To the best of our knowledge, this study represents the first effort to examine any pressurized solid using XRS at the fluorine K-edge.

EXPERIMENTAL

Two experiments were performed. For the first experiment, a premachined beryllium gasket (~3 mm diameter and 1 mm initial thickness) were each lightly pre-indented to ~60 μm thickness using a Paderborn-style diamond anvil cell (DAC) with two aligned and opposing 400 μm culet diameter diamonds. A hole, ~100 μm in diameter, was drilled into the indented center via electric discharge machining.

A 50/50 by volume mixture of KBF₄/KClO₄ powder of >99% purity (Alfa Aesar® for each constituent) was first ground in a mortar and pestle and then introduced into the second empty gasket hole along with a small (~10 μm diameter) ruby crystal for pressure measurement and the sample was pressurized to ~3 GPa.

For the second experiment, KBF₄ powder was placed on Kapton tape and sealed to serve as a reference. No pressure transmitting medium was used in these

studies to maximize our signal, and all measurements were conducted at room temperature. The Paderborn-style DAC used for pressurization of the mixed sample has a wide solid angle aperture perpendicular to the diamond-diamond axis for high collection efficiency of inelastically-scattered x-rays (11).

Our experiments were performed at the High Pressure Collaborative Access Team's (HP-CAT's) 16 ID-D beamline located at the Advanced Photon Source (APS) of Argonne National Laboratory. The diamond cell was mounted in the beamline so that the x-ray beam axis traversed the sample through the beryllium gasket (i.e. the diamond-diamond axis was oriented in the vertical direction).

A silicon (111) double crystal monochromator filtered x-rays of energy near 680 eV above the elastic scattering energy, which were then focused down to 30 μm in the vertical direction and 60 μm in the horizontal direction at the sample using Kirkpatrick-Baez mirrors. The inelastically scattered x-rays were collected by 17 curved Si (555) analyzers which were mounted on a Rowland circle in the vertical plane and set at a scattering angle of 25° relative to the incident x-ray beam axis. The analyzer array refocused the inelastic signal onto a Si detector (Amptek®) for data collection. In a typical data set, the analyzer is fixed in energy, and the incident beam energy is scanned using the monochromator. As is typical with these experiments, data collection took roughly 1-2 hours/spectrum, (20 seconds per energy channel). Roughly 8 scans were taken for each sample. The overall resolution of the spectrometer was ~1.4 eV.

RESULTS

Within each manifold of the two data sets, the spectra were combined and averaged. Color changes were observed in the mixed sample after irradiation of the consistent with the release of fluorine (greenish-yellow color) in the pure KBF₄ and KBF₄/KClO₄ mixture and with the release of oxygen (yellow color) in the KBF₄/KClO₄ mixed sample. Figure 2 displays a photo of the post-irradiated KBF₄/KClO₄ mixed sample.

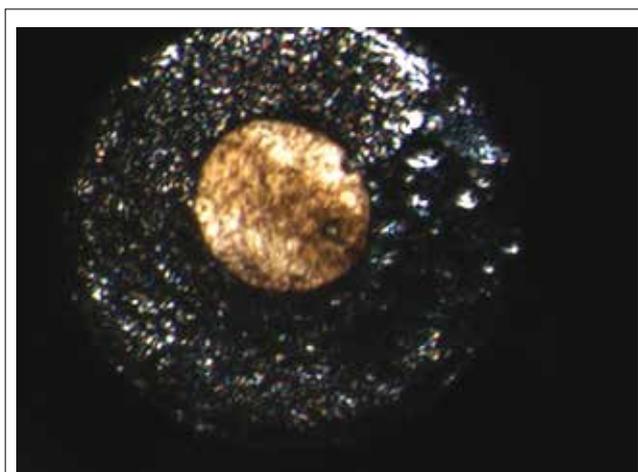


Figure 2. Photograph of the irradiated KBF₄/KClO₄ mixed sample after ~8 hours of irradiation as viewed through one of the diamonds at ~3 GPa of pressure. A faint darkened/chemically-reacted band passes through the sample at an angle of -45° which shadows the path of the x-ray beam through the gasket and sample. A ruby sphere for pressure measurement is located in the band at the 4 o'clock position.

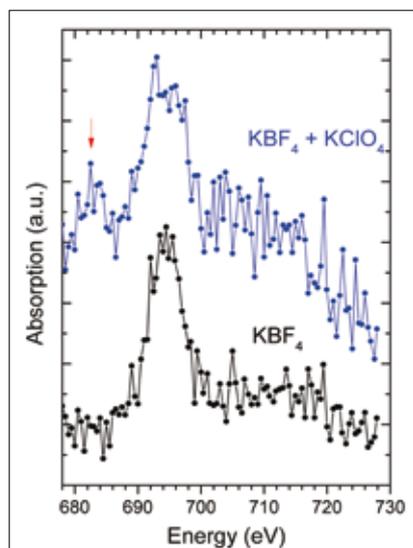


Figure 3. XRS spectra of KBF₄ (bottom trace) and an irradiated mixture of KBF₄+KClO₄. The feature near 682 eV in the upper trace represents OF₂ that was synthesized via x-ray irradiation. Figure 3. XRS spectra of KBF₄ (bottom trace) and an irradiated mixture of KBF₄+KClO₄. The feature near 682 eV in the upper trace represents OF₂ that was synthesized via x-ray irradiation.

We present the XRS results in Figure 3 below. In the KBF₄/KClO₄ mixed sample (top trace), two, possibly three peaks, are evident centered near 682 eV after roughly 8 hours of irradiation. The largest peak near 682 eV is likely the 5a₁σ*(O-F) transition (12). The second peak near 684 eV is likely the 4b₂σ*(O-F) transition. This coincides with an observed peak reported near 685 eV in an EELS study of OF₂ in the gaseous phase (13).

The peaks centered near 696 eV represent a mixture of OF₂, F₂, unreacted KBF₄ and possibly KF (12).

No such peak is observed in this 682 eV region in the pure irradiated KBF₄ sample which has a series of broadened peaks centered near 694 eV.

DISCUSSION

We note that both F₂ and OF₂ are gases at room temperature and pressure. Our studies were of fluorine and oxygen producing compounds which are in the solid state which were loaded into confining and/or pressurizing containers. Thus, accurate comparisons with earlier reported EELS spectra of F₂ and OF₂ are not possible. Nevertheless, we present evidence of the formation of new peaks only after adding, pressurizing, and irradiating a mixture of two compounds which have been shown, based on prior reports (6, 14), to release O₂ and F₂ respectively upon irradiation. This suggests that we synthesized OF₂ in our mixed sample by simultaneously releasing molecular oxygen and fluorine via x-ray irradiation and, then reacting the two products via: $O_2 + 2F_2 \rightarrow 2OF_2$.

CONCLUSION

By irradiating a mixture of KBF₄ and KClO₄ with highly ionizing, highly penetrating, and highly focused hard x-rays, and interrogating the fluorine edge via x-ray Raman spectroscopy, we have produced further conclusive evidence for the formation of OF₂ via useful hard x-ray photochemistry that confirms our earlier study (6). By demonstrating that we can harness hard x-rays to initiate novel and acatalytic chemistry (including the ability to produce reactant molecules *in situ*), we are

hopeful that *hard x-ray photochemistry* (9) can be used in the future to synthesize more complex compounds under extreme or isolated conditions.

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ABOUT THE AUTHOR

Michael Pravica is a professor of physics at the University of Nevada Las Vegas. He received his doctoral and masters degrees from Harvard and his undergraduate degrees from Caltech. As an experimentalist, he studies the behavior of matter subjected to extreme conditions and is developing useful hard x-ray photochemistry.

