A novel method for generating molecular mixtures at extreme conditions: The case of fluorine and oxygen.

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Abstract. We have successfully created a segregated mixture of molecular fluorine and oxygen at high pressure in a diamond anvil cell (DAC) via useful hard x-ray photochemistry. A keyhole-like sample chamber was created in a stainless steel gasket to hold two segregated powders of potassium tetrafluoroborate (KBF_4) and potassium perchlorate ($KClO_4$) respectively in each hole at a pressure of ~3.0 GPa. Both holes were individually irradiated with synchrotron hard x-rays to release molecular fluorine and molecular oxygen, respectively. Upon irradiation of the hole containing KBF_4 molecular fluorine appeared (as evidenced via Raman spectroscopy) near the region of irradiation. The second hole containing $KClO_4$ was then irradiated and reddish-orange O_2 was observed to form. Oxygen was observed to diffuse throughout both holes. There is some evidence that oxygen difluoride (OF_2) was formed in the hole originally containing the KBF_4.

Introduction

We have recently developed a novel method to create a segregated mixture of hydrogen and oxygen at extreme pressures (~3 GPa) in a diamond anvil cell (DAC) and partially react the two molecular species to form water via irradiation by hard x-rays [1]. Interestingly, oxygen was observed to diffuse [1] throughout the segregated sample region whereas hydrogen stayed largely localized in the region of irradiation of the ammonia borane portion of the sample [1]. The fact that the hydrogen and oxygen only appeared to react to form water in the presence of x-rays at high pressure is interesting and useful from a chemical control perspective [1-2]. In addition, the ability to investigate the effect of chemical mixtures of simple molecules (e.g. detonation products) on vibrational frequencies/intermolecular potentials is also of great interest.

We have also recently demonstrated the ability to produce molecular fluorine via hard x-ray irradiation of C_6F_{14} [3]. Fluorine has the highest known electronegativity of any element and thus, from the standpoint of developing novel chemistry under extreme and/or isolated conditions, the ability to irradiate a benign/nonreactive sample to produce highly reactive fluorine, at will, would be highly advantageous. In this study, however, we sought an alternative to C_6F_{14} [1] as an F_2 source as it is a liquid at ambient conditions and thus more difficult to segregate from another chemical compound. Our goal was to create a segregated mixture of two compounds – one oxygen producing and the other fluorine producing which are most easily accomplished by using powders/solids. We have observed that the decomposition process appears most readily in sp^3-bonded systems [3-4] and thus reasoned that KBF_4 might have similar behavior to C_6F_{14} in releasing molecular fluorine. Thus, we sought to study what would happen when two relatively non-reactive (as long as no water is present) powders ($KClO_4$ and KBF_4) were combined into a two-hole ("keyhole") chamber, pressed, and irradiated in the desire to release F_2 and then O_2 (via $KClO_4 + h\nu \rightarrow KCl + 2O_2$ [5]) with the possibility of reacting the two simple molecular species to form OF_2 just as we had earlier formed H_2O [1-2]. We were also interested is comparing the molecular diffusion of F_2 and O_2 under extreme conditions [6].

Experimental

A Japanese-style symmetric DAC with 300 µm-culet type II Raman-quality ultralow fluorescence diamonds was used to preindent a 250 µm thick stainless steel gasket to ~ 80 µm thickness. The preindented gasket was then laser drilled using the laser drilling facility at sector 16 of the High Pressure Collaborative Access Team at the Advanced Photon Source. Two somewhat offset and overlapping holes (each with a diameter 150 µm) and a connecting tunnel were laser drilled with a connecting opening to produce the sample cavity (see Figure 1). Thermally-relieved ruby spheres each of diameter ~20 µm were placed into each drilled hole for pressure measurement. White potassium perfluoroborate powder (Sigma Aldrich > 99%) was ground in a mortar and pestle and placed in one gasket hole under an inert argon atmosphere using the glovebox within sector 16. Similarly ground $KClO_4$ powder (Sigma Aldrich >99%) was manually introduced into the other hole and the combination was sealed and pressurized to ~3.0 GPa which was confirmed in both holes. This pressure was chosen so that any molecular fluorine would be in the solid state at room temperature [7]. We should clarify, however, that in our unique experiments, we create out-of-equilibrium states of matter where the mobile product (usually a gas a room temperature and pressure) may be in an interstitial or bulk form [6] and thus, conventional phase static high pressure diagrams may be invalid at least until the sample better-equilibrates. Our experiment was performed at the 16 ID-D beamline. Monochromatic x-rays of ~10 keV in energy served as the irradiation source. Raman spectra were acquired before and after irradiations utilizing an exciting diode-pumped laser (Coherent®) that operated at a 532 nm wavelength. Raman scattered light was collected with a Triax 550® spectrometer (resolution ~1 cm^{-1}) that was attached to a Princeton Instruments® nitrogen-cooled CCD detector in the Raman facility at sector 16. Irradiations were performed through the diamonds (i.e. parallel to the diamond-diamond axis) and all measurements were conducted at room temperature.

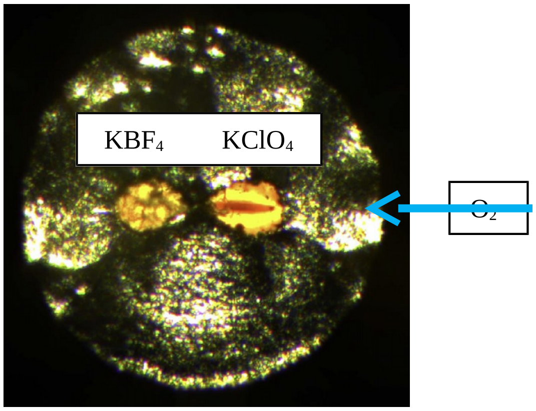

FIGURE 1. Photo of the “keyhole” pressurized to near 3GPa as viewed through one of the sealing diamonds. The hole on left contains KBF_4 that has been irradiated and the hole in the right of the photo contains irradiated $KClO_4$. There is a bridge between the holes that is partially closed down during pressurization but has not sealed shut. The red/orange color in this region comes from molecular oxygen that has been released during irradiation of this hole. The image on the right was taken in transmission as observed through the diamonds. X-ray induced damage can be readily observed in the $KClO_4$ and is indicative of the beam shape available at the 16 ID-D beamline during the experiment.

Results

The DAC was pressurized to 3 GPa initially, as measured in both holes. The connecting tunnel closed down somewhat but not completely. Some of the KBF_4 extruded somewhat into the second $KClO_4$-containing hole during pressurization/sealing due, presumably, to differential compressibility of the two different samples as was observed earlier [1]. However, despite this occurrence, the regions remained largely chemically-segregated as observed via Raman spectroscopy. The hole containing KBF_4 was first irradiated with a 50 µm x 20 µm x-ray beam for ~1 hour turning the sample somewhat yellowish. Molecular fluorine was observed in the center of the hole via the presence of the fluorine of vibron of α-F_2 (see Figure 2) near 903 cm^{-1} [7]. The second hole containing $KClO_4$ was then subsequently irradiated with x-rays for an hour and orange-red molecular oxygen [8] was observed to form in the region of the sample containing (see Figures 1 and 3) and was observed to have diffused throughout the entire sample regions (both holes) as has been observed in earlier experiments [1, 6]. However, it should be noted that the color change from translucent to orange was only observed in this sample hole containing $KClO_4$ suggesting a higher concentration of oxygen in this hole (as opposed to the other hole KBF_4 – containing hole), which was confirmed via Raman spectroscopy.

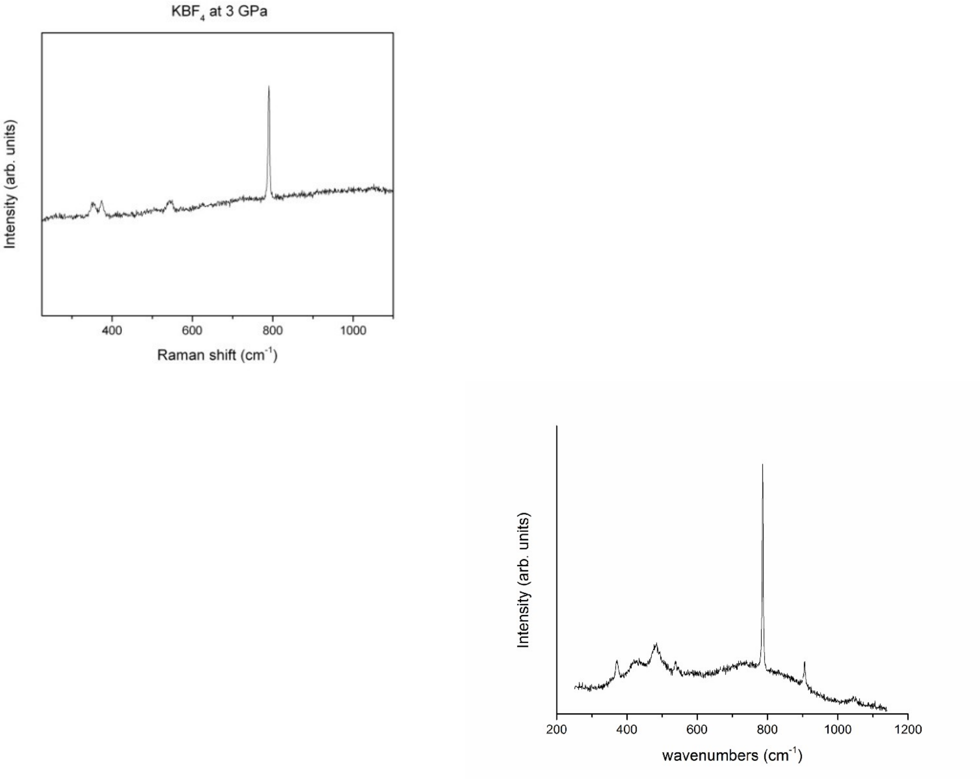

FIGURE 2. Raman spectral traces from center of the hole containing KBF_4 pre- (left) and post-irradiation (right). The molecular fluorine vibron is evident in the small but sharp peak near 903 cm^{-1} in the figure on the right.

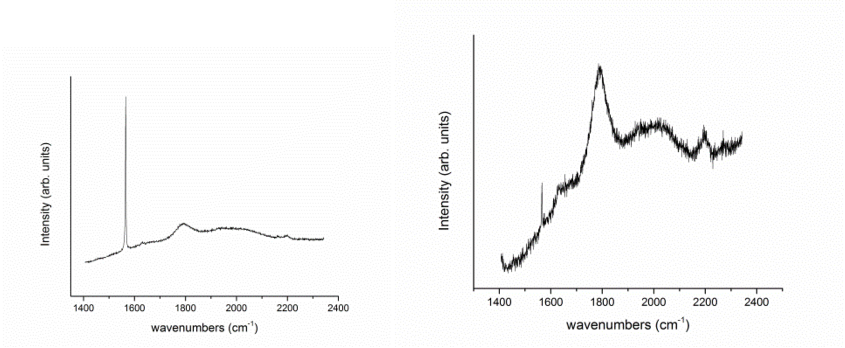

FIGURE 3. Post-irradiation Raman spectrum in the center of the $KClO_4$ hole (left) and a spectrum of the opposite end of the KBF_4-containing hole (right). The oxygen vibron is prominent in the $KClO_4$-bearing irradiated hole. A small but sharp and blue-shifted oxygen vibron appears in the near 1590 cm^{-1} presenting evidence that oxygen has permeated throughout both sample regions.

In the spectrum displayed in Figure 2 (which was taken after irradiation in the center of the KBF_4-containing hole), the large mode near 780 cm^{-1} is assigned to the ν_1 vibration of KBF_4 [9-10] and the left-most peak seen evident near 370 cm^{-1} is assigned to the ν_4 mode [9-10].

In Figure 4, a Raman spectrum from the region near the mouth of the KBF_4-containing hole is displayed. The large and sharp peak near 780 cm^{-1} indicates the presence of some unirradiated KBF_4. Two broad and new peaks near 465 cm^{-1} and 930 cm^{-1} may be associated with the ν_2 (for the lower energy peak) and the ν_1 and 2 ν_2 modes (for the higher energy peak) of solid OF_2 [11].

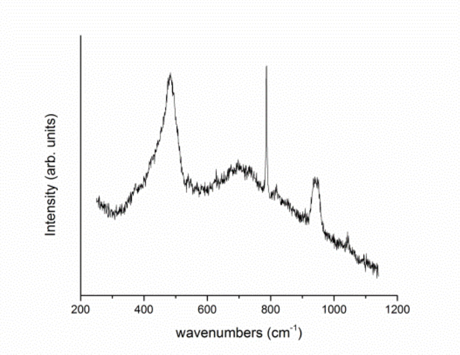

FIGURE 4. Possible evidence of the formation of OF_2 in the KBF_4-containing hole. There are two broad lines near 465 cm^{-1} and 930 cm^{-1} that are likely associated with the ν_2, and ν_1 and $2\nu_2$ modes of solid OF_2 respectively [11].

Discussion

Our goals in performing this novel experiment entailed the production of a mixture of F_2 and O_2 and determine if the two species would diffuse and react under extreme conditions via useful hard x-ray induced chemistry [2-3]. The fluorine vibron and oxygen vibron were both observed indicating that F_2 and O_2 were produced. However, as in our earlier study [1], only the molecular oxygen appears to readily diffuse under high pressure in part due to the fact that it is likely in the liquid state [12] at 3 GPa. We have some evidence that OF_2 was created under x-ray irradiation but will need to follow this up with infrared measurements.

Conclusion

We have successfully produced F_2 from KBF_4 via useful hard x-ray photochemistry. We have produced a mixture of F_2 and O_2 and observed that fluid O_2 diffused into both sample chambers. We have some evidence that OF_2 was produced which would represent another demonstration that useful hard x-ray photochemistry [2-3] can synthesize compounds as well as decompose them.

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