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Fluorine chemistry at extreme conditions: Possible synthesis of HgF₄

Michael Pravica,^{1*} Sarah Schyck,¹ Blake Harris,¹ Petrika Cifligu,¹
Eunja Kim,¹ Brant Billinghamurst²

By irradiating a pressurized mixture of a fluorine-bearing compound (XeF₂) and HgF₂ with synchrotron hard x-rays (> 7 keV) inside a diamond anvil cell, we have observed dramatic changes in the far-infrared spectrum within the 30–35 GPa pressure range which suggest that we may have formed HgF₄ in the following way: XeF₂ $\xrightarrow{h\nu}$ Xe + F₂ (photochemically) and HgF₂ + F₂ → HgF₄ (30 GPa < P < 35 GPa). This lends credence to recent theoretical calculations by Botana *et al.* that suggest that Hg may behave as a transition metal at high pressure in an environment with an excess of molecular fluorine. The spectral changes were observed to be reversible during pressure cycling above and below the above mentioned pressure range until a certain point when we suspect that molecular fluorine diffused out of the sample at lower pressure. Upon pressure release, HgF₂ and trace XeF₂ were observed to be remaining in the sample chamber suggesting that much of the Xe and F₂ diffused and leaked out from the sample chamber.

I. Introduction

Mercury and cesium have been predicted to behave as a transition metal [1, 2] and p-block element respectively [2, 3] at high pressure (within the 1 Mbar range) in the presence of fluorine and thus have higher oxidation states enabling sharing/transfer of electrons from the inner shells (i.e. below the valence levels) of the elements as fluorine atoms are brought closer to the metals via high pressure. As the most electronegative element, there are a number of challenges associated with loading highly reactive and toxic molecular fluorine into a diamond anvil cell which is likely the primary reason why

there was only one published study of the material at high pressure (> 1 GPa) to the best of our knowledge [4]. In an effort to develop fluorine chemistry at extreme conditions, we have utilized hard x-ray induced photochemistry [5] to release molecular fluorine *in situ* inside a sealed and pressurized diamond anvil cell by irradiating a relatively inert and easy-to-handle, powdered or liquid (and thus easy to load) fluorine-bearing compound such as perfluorohexane (C₆F₁₄) [6], potassium tetrafluoroborate (KBF₄) [7] or XeF₂. The fluorine-bearing compound is then irradiated with x-rays that are of sufficient energy to penetrate the confining diamonds (or surrounding gasket) [7] which are typically in the hard x-ray range (> 7 keV). As long as we are at a pressure above the solidification pressure of fluorine (2 GPa), the released atomic or molecular fluorine from irradiation is now confined in the sample hole and thus available for chemical reaction.

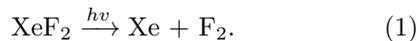
In the present study, we sought to verify the

*E-mail: pravica@physics.unlv.edu

¹ High Pressure Science and Engineering Center (HiPSEC) and Department of Physics, University of Nevada Las Vegas (UNLV), 89154-4002 Las Vegas, Nevada, USA.

² Far-IR beamline, Canadian Light Source, 44 Innovation Blvd, Saskatoon, SK S7N 2V3, Canada.

predictions of transition metal behavior of Hg by mixing a fluorine-bearing compound (XeF_2) with HgF_2 . Fluorine would be produced via x-ray irradiation of XeF_2 via the following photochemical reaction:



The molecular fluorine would then be available to react with HgF_2 in the following way:



under high pressure. The goal of this effort, then, was to ascertain if any molecular changes occurred after irradiation and then after further pressurization. As our samples are typically very fluorescent after irradiation, we chose infrared spectroscopy as the means to interrogate bonding changes within our sample. As the confined sample was ~ 3 nano liters, we used a bright synchrotron hard x-ray source and synchrotron infrared source to produce fluorine *in situ* and to spectroscopically investigate our post-irradiated sample respectively.

II. Experimental

Due to the high reactivity of both HgF_2 and XeF_2 with air and water, loading of the sample was performed inside a Ar-backfilled glovebox located at the High Pressure Collaborative Access Team's sample preparation facility at the Advanced Photon Source of Argonne National Laboratory. A rhenium gasket was preindented to $20 \mu\text{m}$ thickness (from $250 \mu\text{m}$ initial thickness) using a symmetric-style Diamond Anvil Cell (DAC) with diamonds that each had a culet diameter of $\sim 300 \mu\text{m}$ and were IR-transmitting type I quality. A sample hole of diameter $\sim 80 \mu\text{m}$ was laser drilled in the gasket [8]. Powdered xenon difluoride (Sigma Aldrich $> 99\%$) was pulverized with HgF_2 (Sigma Aldrich $> 99\%$) in a 50/50 mixture by volume and was loaded via spatula into the gasket hole. One thermally-relieved ruby (for pressure measurement) was introduced into the sample which was pressurized to 10 GPa. No pressure-transmitting medium was used in our experiments and all were performed at room temperature. Raman spectroscopy was performed on the sample to verify that XeF_2 was present in the loaded and pressurized sample.

The loaded sample was then irradiated with "white" x-rays produced at the 16 BM-B beamline at the Advanced Photon Source (APS). The beam was ~ 30 microns in diameter. The HgF_2 and XeF_2 mixture was irradiated for more than five hours at pressures above 10 GPa to avoid any material losses triggered by the X-ray induced decomposition of XeF_2 . XRD patterns of the sample were taken at the 16 ID-B using monochromatic x-rays that were collected by a MAR345® image plate detector. We also note that no irradiation-induced changes in pure HgF_2 were observed at any pressure in separate experiments. Thus, only XeF_2 is photochemically-affected by x-rays.

The irradiated sample was then transported to the 02B1-1 far-infrared (far-IR) beamline of the Canadian Light Source (CLS) where IR Spectroscopy measurements at various pressures were carried out *in situ* inside the DAC. Pressure was measured using a homemade ruby-fluorimeter constructed by our group located on site at the CLS. The IR collection system consisted of a plexiglass enclosure housing the DAC and collection optics which was in front of the Fourier Transform-IR system and was continuously purged from water vapor (measured by a humidity sensor) using positive pressure nitrogen gas blowoff from a liquid nitrogen dewar. A horizontal microscope system collected far-IR spectra. The IR beam was redirected from the sample compartment of a Bruker IFS 125 HR® spectrometer to within the working distance of a Schwarzschild objective which focused IR light onto the sample. A similar light focusing objective placed behind the sample was used to collect the transmitted light, directing it onto an off-axis parabolic mirror which refocused the IR light into an Infrared Laboratories® Si bolometer. The spectrometer was equipped with a 6-micron mylar beamsplitter. The data was collected using a scanner velocity of 40 kHz, 12.5-mm entrance aperture, with a 1 cm^{-1} resolution. The Si bolometer was set for a gain of $16\times$. Interferograms were transformed using a zero filling factor of 8 and a 3-term Blackman Harris apodization function.

FT-IR spectral scans typically required 15 minutes to acquire and all measurements were performed at room temperature.

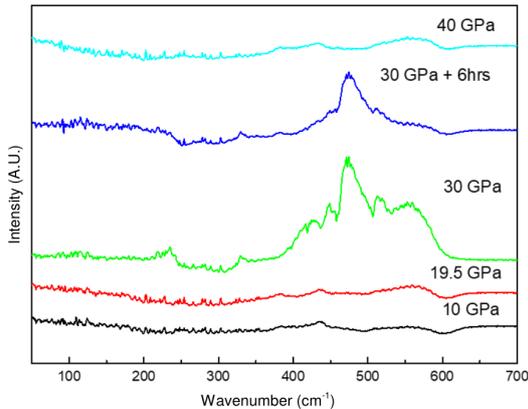


Figure 1: Transmission far-IR spectra of HgF_2 and XeF_2 mixture pressurized up to 30 GPa and held at 30 GPa for 6 hours then pressurized to 40 GPa. As the pressure is increased beyond 19.5 GPa, a broad multiplet of spectral lines appear near 474 cm^{-1} and one smaller mode appears near 234 cm^{-1} . The patterns disappear in the 40 GPa spectra.

III. Results

After initial loading at the APS, the sample possessed a greenish yellow tint demonstrating the presence of HgF_2 . After further pressurization at the CLS, the sample significantly darkened. We present our IR spectral data in the $35\text{--}650\text{ cm}^{-1}$ range in Fig. 1. We first compressed the sample from 10 GPa up to 40 GPa recording spectral patterns along the way. As is evident from the figure, a peak near 235 cm^{-1} and a multiplet of peaks centered near 474 cm^{-1} appear around 30 GPa. We allowed the sample to remain at 30 GPa for 6 hours and then took another IR spectrum to examine stability of the new peaks with time. The 235 cm^{-1} peak vanished or was severely diminished within the signal to noise of our system and the multiplet centered around 474 cm^{-1} largely disappeared or severely diminished with the exception of the peak itself. Upon further pressurization to 40 GPa, the highest pressure we subjected the sample to, the patterns completely disappear.

The sample pressure was then reduced to 35 GPa (Fig. 2, curve a) to ascertain if the observed peaks returned which they did as evidenced in the 32 GPa pattern in Fig. 2, curve b. Pressure was again increased to 35 GPa and the pattern again disap-

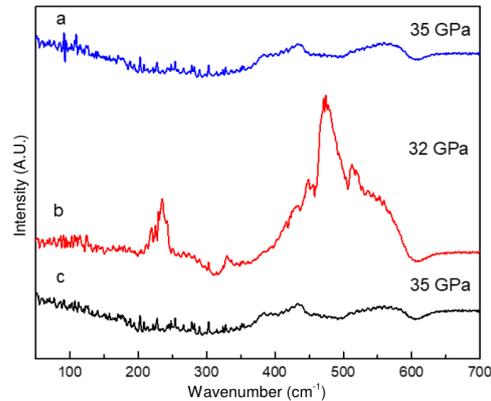


Figure 2: Transmission far IR spectra of the irradiated XeF_2 and HgF_2 mixture as the sample was decompressed from 35 GPa (trace a) to 32 GPa (trace b) and then recompressed to 35 GPa (trace c) demonstrating reversibility of the peak structure at 32 GPa. This pressure-cycled sequence occurred after the first viewing of the feature around 30 GPa present in Fig. 1.

peared (Fig. 2, curve c). Pressure was reduced to just above ambient ($\sim 1\text{ GPa}$) and the sample returned to its original white/yellow appearance before irradiation (white). Figure 3 displays photos of the sample at various stages. Raman spectroscopy was performed upon returning the sample to the Pravica Raman facility at UNLV indicating that only HgF_2 and a residual amount of XeF_2 remained in the sample chamber. X-ray diffraction (XRD) patterns taken of the sample before irradiation and after irradiation, compression and decompression to ambient conditions (see Fig. 4) further verifies the claim that the Xe and F_2 (produced via irradiation of XeF_2) leaked out from the gasket once the pressure was reduced to near ambient conditions. There is no indication that the rhenium gasket suffered any significant chemical reaction from the F_2 (see Fig. 4). We have observed this behavior of little or no diffusion of F_2 in our samples in prior experiments that produced F_2 from KBF_4 leading to little or no gasket damage [10] and no discernible reaction with the diamonds [4].

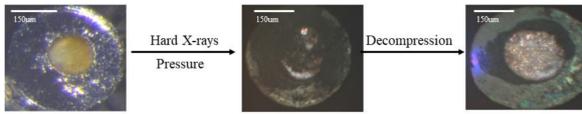


Figure 3: Progression sequence of the sample. The first photo on the left represents the mixed $\text{XeF}_2 + \text{HgF}_2$ sample near 10 GPa after sample loading. A yellowish hue is evident due to the presence of HgF_2 . The second (middle) photo illustrates darkening of the sample after irradiation and pressurization to 25 GPa and persisted in this visual state until 40 GPa, the highest pressure in this study. The final photo on the right demonstrates that the sample has returned to its original appearance after reducing pressure to ambient conditions.

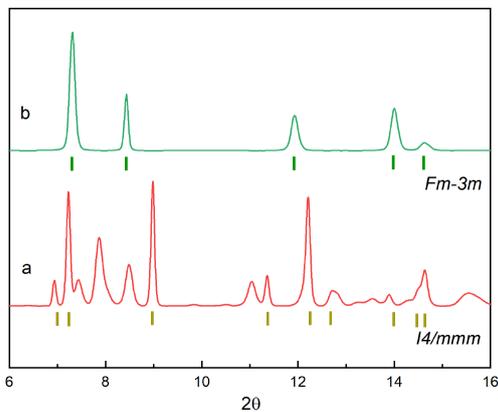


Figure 4: XRD patterns of the $\text{HgF}_2/\text{XeF}_2$ mixture (a) before x-ray irradiation and (b) after irradiation, pressurization, and decompression indicating that the XeF_2 leaked out from the gasket in the form of Xe and F_2 (produced from the initial x-ray irradiation) leaving only HgF_2 in the sample chamber in the $Fm-3m$ crystalline structure. The vertical olive green bars in (a) represent the tetragonal crystal structure of XeF_2 with the $I4/mmm$ space group [11].

IV. Discussion

HgF_4 in the gaseous state has a predicted IR mode (A_{2u}) near 233 cm^{-1} [9] which agrees well with the mode we observed near 235 cm^{-1} though we recognize that our mode was observed in the solid state (not the gaseous state) and is at very high pressure. We suspect that the feature near 474 cm^{-1} is an overtone of the mode near 235 cm^{-1} . Botana *et al.* have calculated stability of HgF_4 in the 38–73

GPa pressure range; that HgF_3 and HgF_4 are both stable from 73–200 GPa; and that from 200–500 GPa, only HgF_3 is the stable compound with Hg in the +3 oxidation state [1]. Seeking to confirm this prediction, we pressurized the DAC into the 30 GPa and higher pressure range. As is apparent from our data, a new compound with mercury appears to form near 30 GPa and then disappears around 35 GPa. The compound forms reversibly with pressure cycling. Upon further reduction of pressure to ambient conditions, the sample turned white (as it was originally before being irradiated). Raman spectroscopy confirmed only the presence of HgF_2 indicating that the Xe and F_2 leaked out from the gasket. The process (irradiation, pressurization and return to ambient) is visually described in Fig. 3.

We note in passing that we performed a purely high pressure mid-IR study of just the $\text{XeF}_2 + \text{HgF}_2$ mixture (see Fig. 5) and found no evidence of any significant spectral changes (with the exception of a phase transition near 5 GPa from HgF_2) demonstrating that x-ray irradiation in combination with high pressure is necessary to produce the interesting features observed in Fig. 2.

V. Conclusions

We have performed a synchrotron far-IR experiment on an irradiated mixture of XeF_2 and HgF_2 pressurized in a DAC. The irradiation was performed to release molecular fluorine inside the sample chamber at high pressure *in situ* thereby obviating the need to load toxic and reactive molecular fluorine inside the diamond cell. Upon further pressurization just above 30 GPa, we observed the dramatic appearance of a peak or peaks centered near 234 cm^{-1} and likely an overtone near 474 cm^{-1} in a narrow pressure range somewhere between 30–35 GPa which appears to be reversible and which appears to correlate with the calculated A_{2u} mode of HgF_4 . Our observation differs somewhat from the predictions of Botana *et al.* of a 38–73 GPa pressure range of stability [1] but given the challenges associated with connecting theory and experiment at high pressure and given the complex chemistry occurring during and after hard x-ray irradiation and at high pressures, our results are nevertheless encouraging.

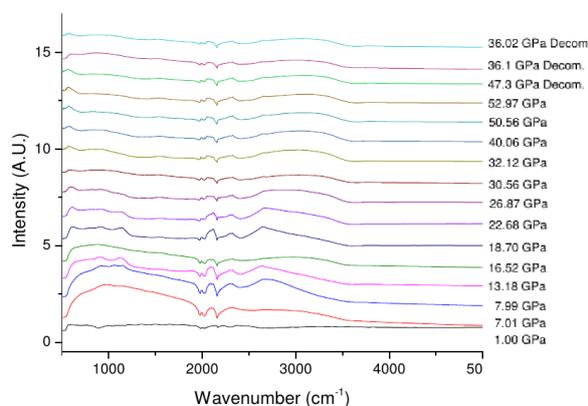


Figure 5: Transmission mid-IR spectra of HgF_2 and XeF_2 non-irradiated mixture pressurized up to 36 GPa.

Upon release of pressure to ambient, the fluorine and Xe produced by the irradiation of XeF_2 likely leaked out and HgF_2 remained inside along with residual XeF_2 . Though far-IR experiments do not by themselves prove the formation of HgF_4 , we are nevertheless encouraged by our results. Further experiments are planned to confirm and further verify our results. We anticipate that this seminal experiment will further encourage development of fluorine chemistry at extreme conditions.

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