

Hexafluorobenzene Under Extreme Conditions

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We report the results from three high pressure experiments on hexafluorobenzene (C_6F_6). In the first experiment, Raman spectra were recorded up to 34.4 GPa. A phase transition from I \rightarrow II was observed near 2 GPa. Near 8.8 GPa, a phase transition to an unreported phase (III) commenced. Above 20.6 GPa, yet another phase was observed (IV). Pressure cycling was employed to determine that below 25.6 GPa, all pressure-induced alterations were reversible. However, at pressures above 20 GPa, dramatic spectral changes and broadening were observed at 25.6 and 34.4 GPa. The sample irreversibly changed into a soft solid with waxlike consistency when pressure was reduced to ambient and was recoverable. In the second experiment, IR spectra were collected up to 14.6 GPa. The phase transition (II \rightarrow III) near 8.8 GPa was confirmed. An angular dispersive x-ray diffraction experiment was conducted to 25.6 GPa. Phase transitions above 1.4 GPa (I \rightarrow II), above 5.5 GPa (II \rightarrow III), above 10 GPa (III \rightarrow IV), and above 15.5 GPa (IV \rightarrow V) were observed. Near 25.6 GPa, long range crystalline order was lost as the x-ray diffraction spectrum presented evidence of an amorphous solid.

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Keywords: Infrared spectroscopy, Raman spectroscopy, diamond anvil cell, high pressure, x-ray diffraction, fluorine chemistry, polymerization

Introduction:

Pravica, et al., “C₆F₆ at extreme conditions”

We have recently demonstrated that *hard x-ray induced photochemistry* [1-2] can be harnessed to release molecular fluorine *in situ* inside a sealed and pressurized diamond anvil cell via synchrotron x-ray irradiation of relatively inert and safe-to-use perfluorohexane (C_6F_{14}) [3]. We have, thus, continued seeking alternative easy-to-load and relatively inert/less reactive compounds that might be feasible sources of highly reactive and toxic molecular fluorine inside a diamond anvil cell. We have also studied ringed hydrocarbons such as cyclopentane [4], benzene [5], cyclohexane [6-7], and cyclooctatetraene [8-9] at high pressure to examine chemical bonding alterations and even polymerization under extreme conditions [5, 8]. In the desire to expand our studies of fluorocarbons (as potential sources of molecular fluorine) and to develop the potential of novel fluorine-based chemistry under extreme conditions, we sought to interrogate hexafluorobenzene or perfluorobenzene (C_6F_6) at high pressure. This aromatic molecule is similar in structure to benzene (see Fig. 1) and thus is interesting to examine in comparison to benzene which we have studied earlier [5] and which has been extensively studied at high pressure [10]. As far as we are aware, there is only one high pressure study [11] of this fundamental and highly symmetric molecule which reported Raman spectra up to 5 GPa. Thus, we sought to contribute further information on this molecular system at far higher pressures.

At ambient temperature, C_6F_6 undergo known phase transitions from the liquid state with pressure (liquid \rightarrow phase I \rightarrow phase II) up to 4.7 GPa [11]. The liquid solidifies into Phase I when slowly compressed beyond 0.3 GPa and then transforms into Phase II somewhere between 2-4 GPa [11]. If, on the other hand, the material is rapidly compressed up to 0.8 GPa, the material goes directly into Phase II [11]. We thus sought

to extend the high pressure ambient temperature phase diagram of this highly symmetric molecule using Raman and, for the first time, x-ray diffraction (XRD) and infrared (IR) methods.

Experimental:

We employed a symmetric-style Diamond Anvil Cell (DAC) with 250 μm thick stainless steel gaskets to pressurize and confine liquid C_6F_6 . The diamonds used each had a culet diameter of ~ 300 μm and were low fluorescence type II quality. The sample-confining gasket was preindented to ~ 50 μm thickness and a sample hole of diameter ~ 100 μm was drilled via electric discharge machining. Liquid C_6F_6 (Sigma Aldrich spectrophotometer grade $> 99\%$) was loaded via a hypodermic syringe into the gasket hole along with one ruby (for pressure measurement) and then the assembly was rapidly closed to seal the sample. No pressure-transmitting medium was used in our experiments and all were performed at room temperature.

The first experiment was performed within the Pravica group Raman facility at UNLV. The laser power source consisted of a Spectra Physics® Ar ion laser tuned to the 514.5 nm laser line set at 100 mW (20 mW at the sample). A Jobin Yvon U1000® spectrometer dispersed the scattered light which was then stored via an Princeton Instruments Spectrum One® detector. The Raman spectrometer instrumental resolution was ~ 1 cm^{-1} . The Rayleigh scattered light was filtered using a Kaiser optics® 514.5 nm holographic notch filter. Acquisitions typically required 60 sec to complete.

The second experiment was performed at the 16 BM-D beamline at the Advanced Photon Source (APS). Fresh liquid C_6F_6 was loaded into a symmetric-style (the same one

used in the Raman experiment) and pressurized. The sample chamber dimensions were similar to those of the first Raman experiment. Monochromatic x-rays of energy 25 keV were used for x-ray diffraction and detected using a Mar 345® image plate detector.

The final experiment sought mid-IR spectroscopic information on C₆F₆ at high pressure and was performed at the Canadian Light Source (using the 01B1-1 mid-IR beamline). The symmetric-style DAC employed in this final study had IR-transmitting diamonds of type IIa quality. The sample chamber dimensions were similar to those of the first Raman experiment except that the preindented gasket thickness was considerably reduced (~15 µm initial thickness) to reduce IR absorption. Pressure was measured using a ruby-fluorimeter located on site at the CLS. Mid-IR spectra were recorded by using a Bruker Vertex 77v/S, Hyperion 3000 IR microscope which possessed a liquid N₂-cooled HgCdTe (MCT) detector. The IR beam was externally focused onto the sample using a nitrogen-purged IR microscope (Brüker IR Scope II® with a Brüker Hyperion Vertex 80v® detector). The mid-IR microscope system generally focuses the IR beam down to 20 µm which is then spatially filtered via a 20 µm diameter circular aperture. One background spectrum was acquired after releasing the original sample between the diamonds and then subtracted from the sample spectra acquired at various pressures.

Results:

Raman Study: Two experiments were conducted. In the first the terminal pressure was 25.6 GPa above which the gasket failed in the attempt to pressurize further and the pressure was reduced to ambient. The second experiment was conducted up to 34.4 GPa and then the pressure was also reduced to ambient. We first present combined stacked

Raman spectra from both experiments in Fig. 2. The ambient spectrum (first trace on the bottom) was taken from a capillary. Three prominent modes are apparent near 370 cm^{-1} (e_{1g} fundamental), 440 cm^{-1} (e_{2g} fundamental or ν_6), and 560 cm^{-1} (a_{1g} fundamental or ν_1) which are in good agreement with ref [12-13] suggesting that we started with pure C_6F_6 . Another weaker mode near 740 cm^{-1} is the $2 e_{1g}$ mode [12]. Some of the modes have been plotted as a function of pressure in Fig. 3. As is typical with molecular crystals, the modal behavior with pressure is complicated.

As pressure is increased, all modes shift toward higher energies as expected. Above ambient, the e_{1g} fundamental mode splits (and shifts) at 0.4 GPa which corroborates the transition from liquid into Phase I observed in ref. 11. At or above 0.4 GPa, two peaks emerge near 100 and 120 cm^{-1} respectively heralding the transition into Phase II [11]. Above 5.7 GPa, a new peak emerges near 420 cm^{-1} . Also, the peak that commenced near 100 cm^{-1} above 0.4 GPa splits in the 8.8 GPa spectrum and the mode near 450 cm^{-1} also begins to split in the same trace. At 12.2 GPa, the three apparent peaks between 420 and 460 cm^{-1} dramatically change and appear to reduce to two modes and alter in relative intensity.

Examining the higher pressure spectral traces, little significant changes are observed until 20.6 GPa. Above this pressure, the spectra notably alter. The pattern at 25.6 GPa has new peaks and the peaks are significantly broadened thus heralding the onset of a some major phase transition, polymerization, or other chemical reaction. There was also evidence of a darkening of the sample at this pressure. After the gasket failed, the sample was decompressed to ambient pressure and the spectra appeared similar to that of the ambient liquid (see Fig. 4).

Another higher-pressure experiment was performed up to 34.4 GPa. At the terminal pressure, the sample further darkened and appeared as a shattered yellow glass. The sample was recoverable upon decompression and had a waxy/semisolid appearance and texture. Figure 5 (left photo) depicts the sample in decompression near 5 GPa (as viewed through one diamond) and then, (right photo) upon total pressure release and removal of one diamond to demonstrate that the transformed sample was still solid and recoverable.

Thus, based on our studies, for pressures above 25.6 GPa, the sample irreversibly altered/reacted and the transformation was irreversible. At or below 25.6 GPa, pressure cycling was reversible. We found no evidence of laser-induced damage of our sample during the course of our studies.

XRD Study: C_6F_6 is a liquid at room temperature and pressure. At 120 K and ambient pressure, it adopts the $P2_1/n(C_{2h}^5)$ crystal structure with 6 molecules/unit cell and $a = 16.82$, $b = 9.17$, $c = 5.76$, and $\beta = 95.8^\circ$ [14]. To the best of our knowledge, there has been no XRD study of this molecular solid at high pressure. The goal for the XRD study was to confirm any phases observed in the Raman study. We present our results in Fig. 4. The sample was pressurized up to 25.7 GPa. Between 5.8 and 10.0 GPa, there is an apparent phase transition as the patterns differ considerably. From 10.0 to 15.1 GPa, the patterns also show evidence of another phase transition. Finally, the diffraction pattern at 25.6 GPa, appears to have polymerized as the peaks are very weak amidst a very broad background. When depressurized to ambient, the pattern exhibited signs of amorphization and therefore no structural order. As an aside, we noted that there was no evidence of sample damage due to x-ray irradiation [1-3].

IR Study: The IR experiment was conducted up to 14.6 GPa. Figure 6 displays stacked IR spectra from a freshly loaded sample. The peaks near 2470 and 2700 cm^{-1} are the $\nu_7 + \nu_{13}$ and $\nu_7 + \nu_{19}$ modes respectively [13]. The modes near 1320 and 1360 cm^{-1} are likely the ν_{13} and $\nu_4 + \nu_{12}$ and $\nu_7 + \nu_{15}$ modes. The broad and strongly absorbing regions near 1000 and 1500 cm^{-1} are associated with a series of strong ν_{20} and $\nu_3 + \nu_{18}$ modes and the ν_{19} mode respectively [13] and are likely saturated in part. The IR spectra largely appear to shift toward higher energies with increasing pressure and two modes near 1340 cm^{-1} combine into one above 8.2 GPa which heralds the phase II \rightarrow III transition. The weak mode near 650 cm^{-1} in the 2 GPa spectrum (ν_{12} vibration [13]) appears to split into two modes at higher pressures. Also, a small peak near 1860 cm^{-1} disappears above 2 GPa. These collective observations likely signify the phase I \rightarrow II transition. In the pressure range of study (0 \rightarrow 14.6 GPa), only two phase transitions were anticipated to be observed (phase I \rightarrow II transition and phase II \rightarrow III transition) and this has been confirmed.

The sample was decompressed to ambient pressure and the IR spectrum appeared similar to the initial low pressure spectrum indicating that all pressure-induced changes were reversible (see Fig. 9) confirming what would be anticipated from our Raman measurements.

Discussion:

Based on the evidence from our three studies, we have confirmed that Phase I appears above 0.3 GPa and the Phase II commences somewhere around 2 GPa. Around 8.8 GPa, the sample enters a new phase (Phase III). Somewhere near 12 GPa, the sample

transitions into Phase IV up to just below 25.6 GPa upon which Phase V appears. In Phase V, crystalline order is lost and some reversible chemical reaction/polymerization occurs. Above 25.6 GPa, however, the reaction is irreversible as the material fully polymerizes. We suspect that the reacted fluorocarbon solid undergoes some sort of Diels Alder reaction where the aromatic rings open up and link with one another to polymerize. Pressure-induced polymerization has been observed in other unsaturated sp^2 -bonded systems. For example, benzene (which has a similar molecular structure to C_6F_6), similarly reacts at high pressure to a recoverable but unknown solid around 24 GPa [10] and into carbon nanothreads when pressurized to 20 GPa for over an hour [15]. Benzene was found to undergo significant bonding alterations at even lower pressures near 14 GPa [5]. We have also observed pressure-induced polymerization in unsaturated cyclooctatetraene (C_8H_8) near 16 GPa [8]. As benzene is considered to be a very chemically-stable molecule [16], it should come as no surprise that high pressures are required for irreversible polymerization to occur. In the present study, we are examining a similar system with different outer bonds (C-F) than the C-H bonds in benzene. As the F atom is far more electronegative than the H atom, the quantum dynamics associated with the inner aromatic ring electrons will differ between the two molecules. Also, C_6F_6 is larger than C_6H_6 . Thus, one might anticipate that a significantly higher pressure would be required to bring the aromatic ring electrons in C_6F_6 close enough to one another to form new sp^3 bonds for polymerization, however, there appears to be relatively little difference in this case (a few GPa).

A recent paper that we became aware of after our measurements were performed describes a calculation that when compressing C_6F_6 , graphite fluoride networks are

thermodynamically more stable above 26.5 GPa and below this pressure, the decomposition products (diamond and CF_4) are more stable [17]. In our study, C_6F_6 not decompose at pressures below 25.6 GPa, presumably because the ambient temperature was insufficient to overcome the thermodynamic activation barriers associated with breaking the sp^2 hybridized bonds to initiate and drive the chemical reaction. However, at higher pressures above 25.6 GPa, we succeeded in initiating a chemical reaction which we presume to be polymerization. Thus, at pressures above 25.6 GPa, a more thermodynamically stable polymeric/reacted phase manifested that may be related to the graphite fluoride sp^3 network that is predicted to be stable above this pressure. The present study, in conjunction with the results from ref. 17, will hopefully aid fluorine chemistry and the effort to create novel polymers at extreme conditions [17]

Conclusion:

We have performed three studies (Raman, XRD, and IR) of an important and fundamental solvent C_6F_6 to continue our studies of fundamental hydrocarbon and fluorocarbon ringed systems including the first reported IR and XRD studies of hexafluorobenzene at high pressure to the best of our knowledge. We have confirmed the presence of Phase I near 0.3 GPa and Phase II near 2 GPa which were observed in an earlier Raman high pressure study [11]. We have observed evidence for three new phase transitions of C_6F_6 : Phase III just above 8.8 GPa, and Phase IV above 12 GPa, and Phase V above 20.8 GPa. Right around 25.6 GPa, there is evidence some sort of reversible reaction and/or polymerization. However, between this pressure and 34.4 GPa, irreversible polymerization occurs whereupon the reacted/polymerized sample can be

recovered at ambient conditions. There was no evidence of radiation induced damage during the course of studies. All changes were induced solely via the application of pressure.

Acknowledgements:

We thank Ferenc Borondics, Scott Rosendahl, and Xia Liu for aid. We thank John Tse and Serge Degrenies for use of their ruby fluorimeter. We gratefully acknowledge support from the Department of Energy National Nuclear Security Administration (DOE-NNSA) under Award Number DE-NA0002912. We also acknowledge support from the DOE Cooperative Agreement No. DE-FC08-01NV14049 with the University of Nevada, Las Vegas. Portions of this work were performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT operations are supported by DOE-NNSA under Award No. DE-NA0001974 and DOE-BES under Award No. DE-FG02-99ER45775, with partial instrumentation funding by NSF. APS is supported by DOE-BES, under Contract No. DE-AC02-06CH11357. A portion of the research described in this paper was performed at the Mid-IR beamline of the Canadian Light Source, which is supported by the Natural Sciences and Engineering Research Council of Canada, the National Research Council Canada, the Canadian Institutes of Health Research, the Province of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan.

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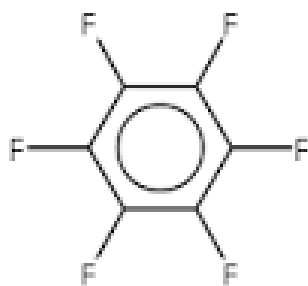


Fig. 1: Perfluorohexane (C₆F₆).

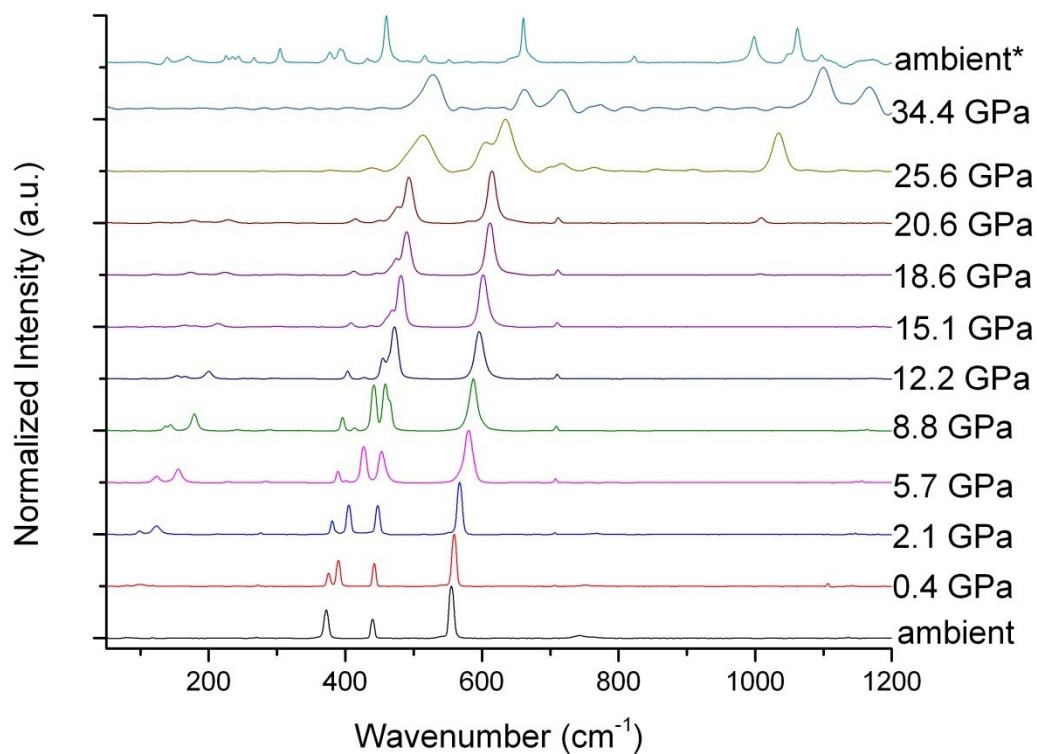


Figure 2: Stacked Raman spectral curves of C₆F₆ at various pressures illustrating some of the phase changes and demonstrating the irreversibility of the sample when pressure cycled down to ambient from a peak pressure of 34.4 GPa. The top trace represents the spectrum after depressurization to ambient and opening of the sample chamber.

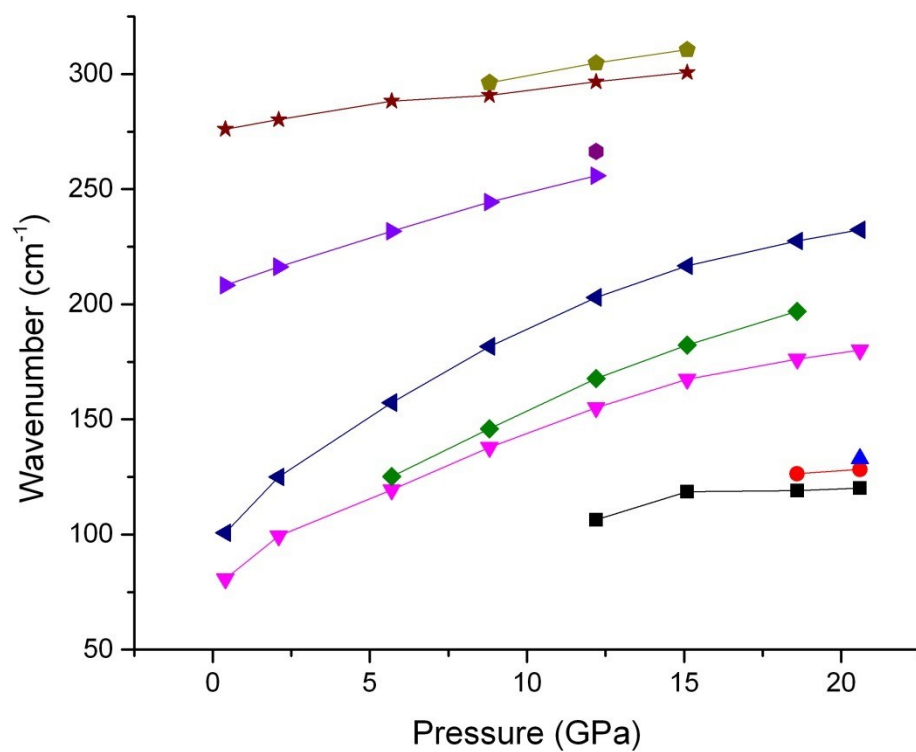


Figure 3: Selected Raman spectral modes plotted as a function of pressure.

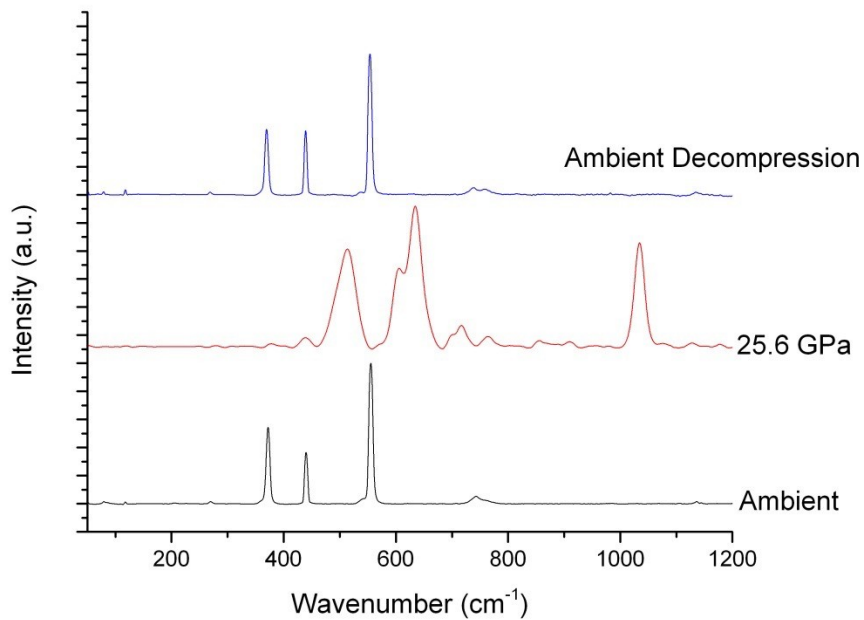


Fig. 4: The C₆F₆ sample was pressurized to 25.6 GPa and then depressurized to ambient. Both ambient Raman spectra taken in the beginning of the experiment and at the end of the experiment appear to be the same suggesting that up to 25.6 GPa, there is no pressure-induced chemical reaction.

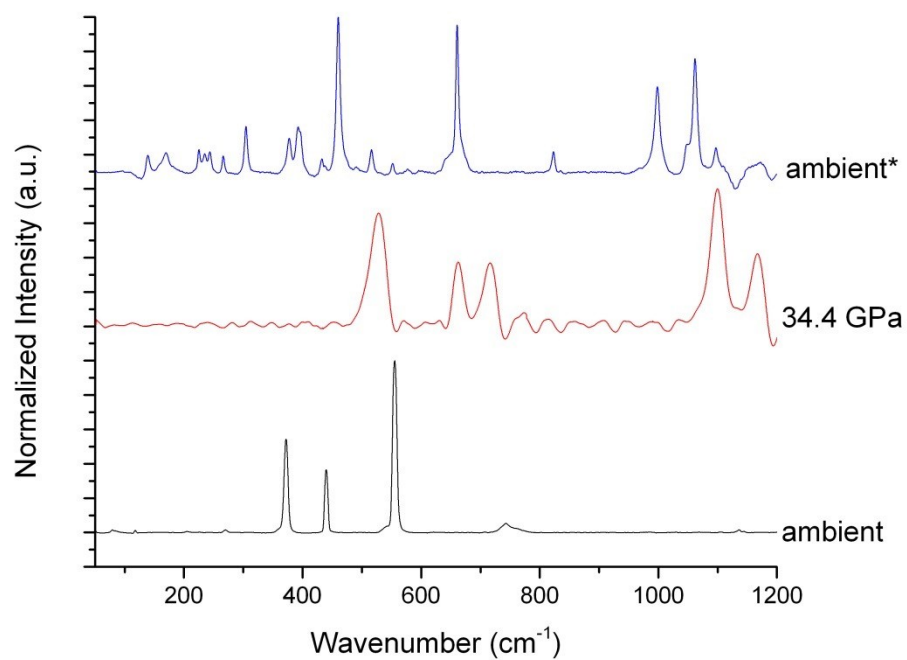


Fig. 5: C_6F_6 sample was pressurized to 34.4 GPa and then depressurized to ambient. The Raman spectra taken after pressure cycling to ambient pressure appears to be considerably different than the ambient pattern before pressurization indicating that somewhere between 25.6 and 34.4 GPa, irreversible chemical reaction/polymerization occurred.

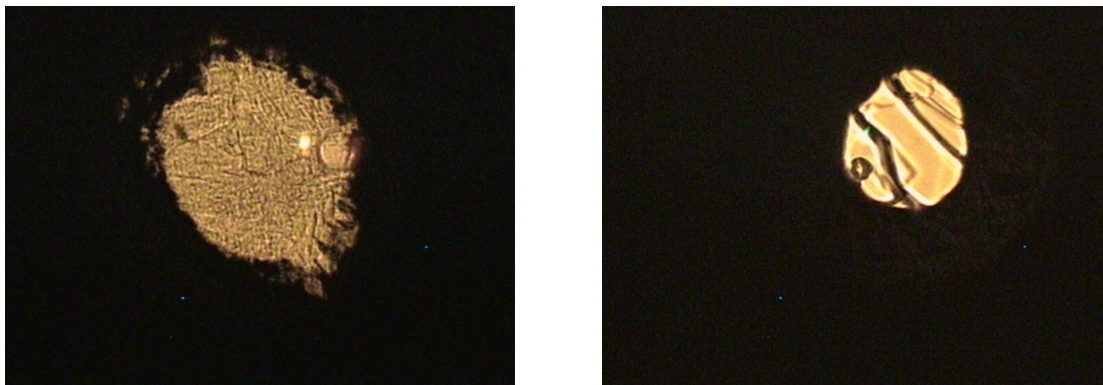


Fig. 6 (Left) Photo of the decompressed sample of C_6F_6 at 5.4 GPa (left) after decompression from 34.4 GPa looking through one diamond. (Right): Photo of the sample after it has been decompressed to ambient and one diamond removed. The sample had waxlike consistency.

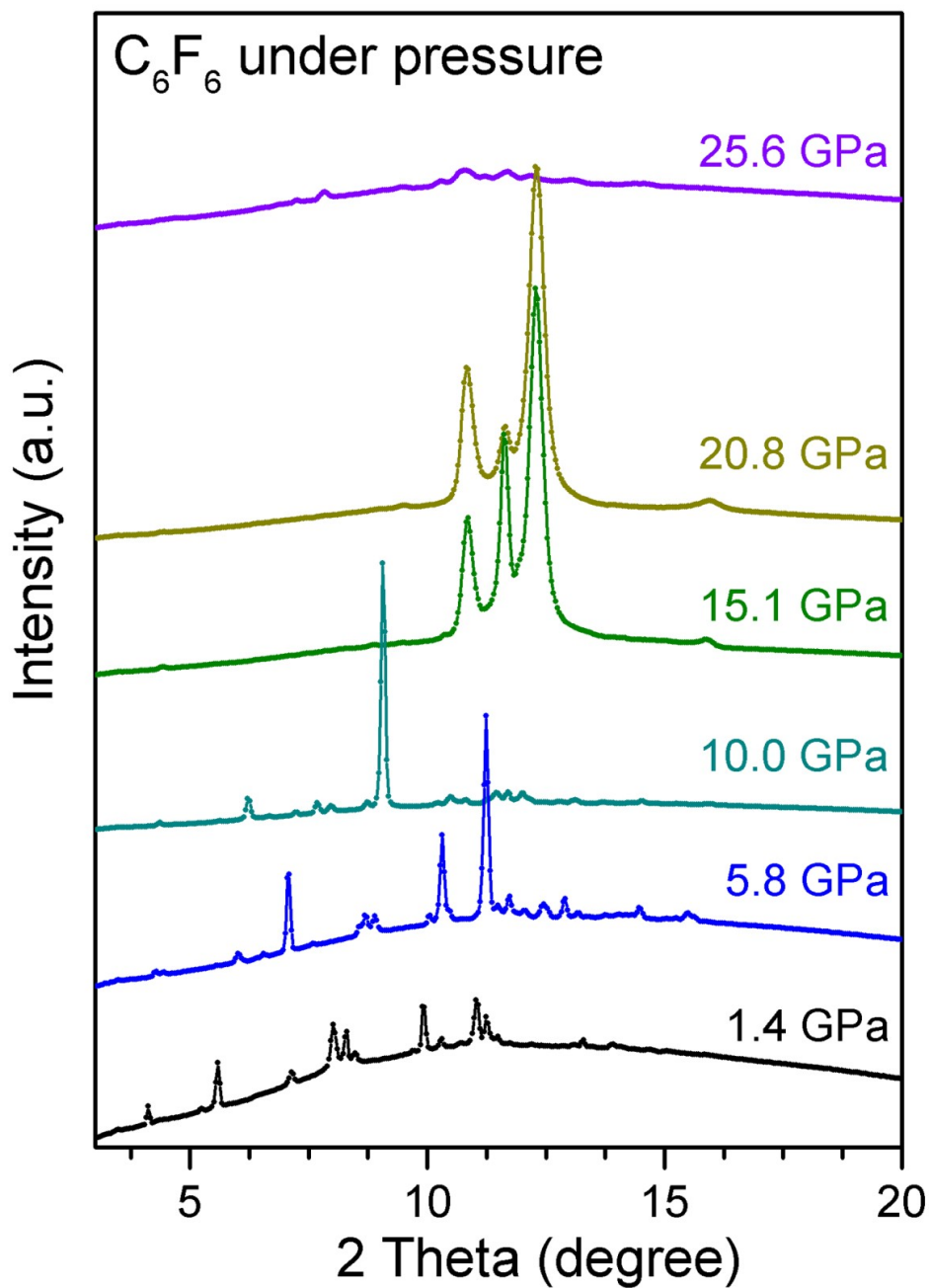


Figure 7: Stacked x-ray diffraction curves of C_6F_6 at various pressures illustrating some of the phase changes, particularly between 5.8 and 10.0 GPa, and between 10.0 and 15.1 GPa. Above 20.8 GPa, most of the crystalline order is lost suggesting disordered polymerization of the sample ($\lambda = 0.49695 \text{ \AA}$).

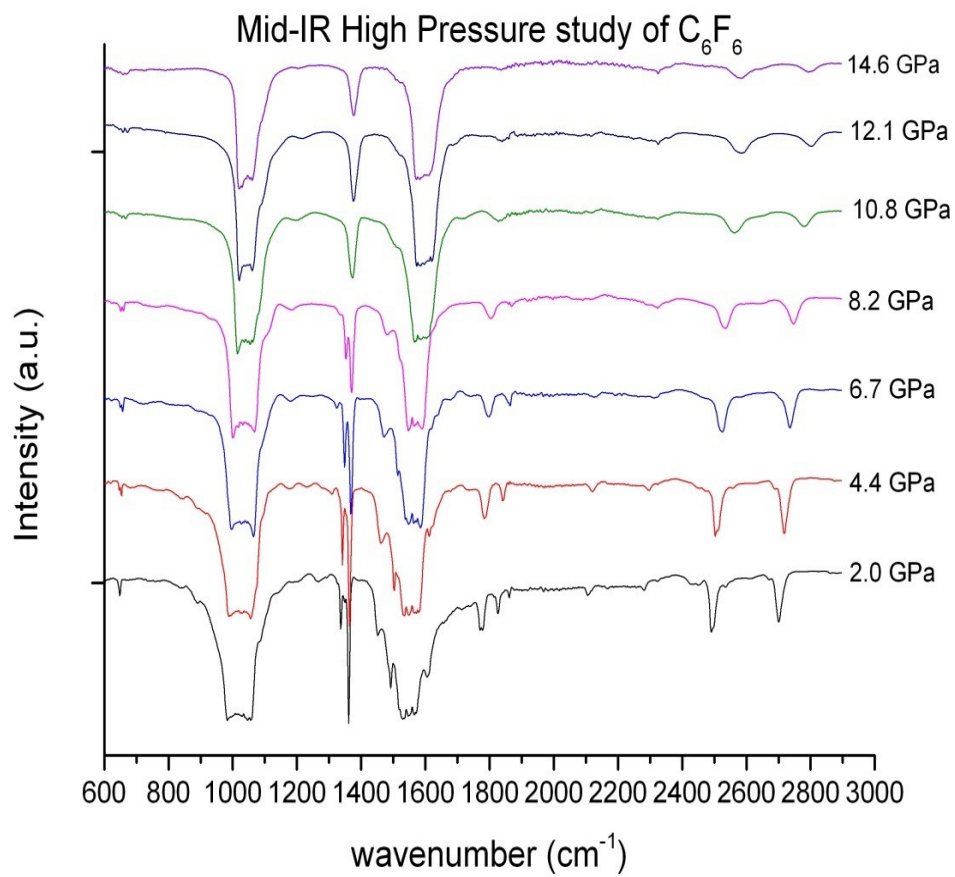


Figure 8: Stacked IR spectra of C_6F_6 at all of the studied pressures.

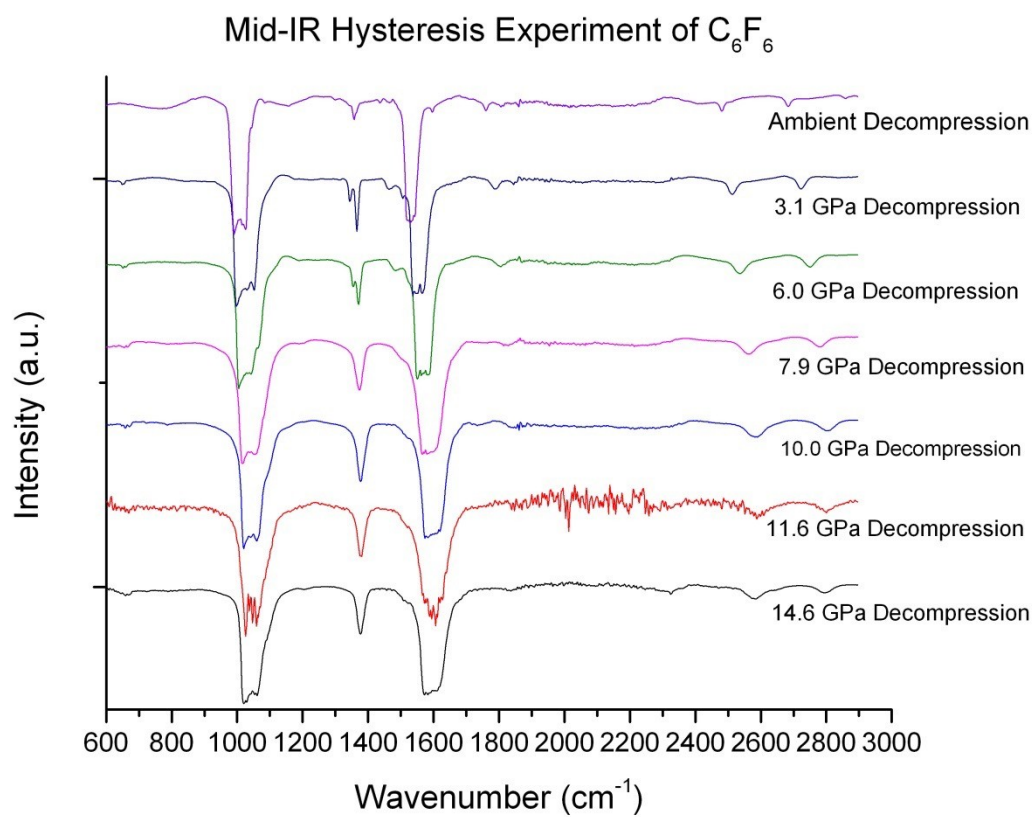


Fig. 9: IR spectra of C_6F_6 plotted during decompression of the sample to ambient pressure demonstrating reversibility of pressurization up to at least 14.6 GPa.