Study of the reaction products of SF₆ and C in the laser heated diamond anvil cell by pair distribution function analysis and micro-Raman spectroscopy

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Abstract

The decomposition of SF₆ in the presence of glassy carbon was induced in laser heated diamond anvil cells at 10 to 11 GPa and 2000 to 2500 K. The reaction products were characterised by synchrotron X-ray diffraction, including high pressure pair distribution function analysis, and micro-Raman spectroscopy combined with atomistic model calculations. The decomposition leads to elemental amorphous helical sulfur and crystalline CF₄-III. Two different sulfur phases, namely helical S_μ and crystalline α-S₈, were observed after recovering the laser heated samples of different experiments at ambient conditions.

Keywords: sulfur hexafluoride, pair distribution function, diamond anvil cell, high pressure

1. Introduction

Chemical reactions of small molecules at extreme pressure and temperature conditions have been studied extensively because the reaction products have interesting chemical, physical and mechanical properties [1, 2, 3]. Well-known examples include the polymerisation of CO₂ [4], N₂ [5] and CO [6, 7].

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Polymerised CO and N₂ for instance are potential high-energy materials [6, 5] and the quartz-like CO₂ polymer is proposed to be a super-hard material [8].

Sulfur hexafluoride, SF₆, is a very stable and inert compound and hence widely used, for example as insulator material in electric equipment [9]. The high-pressure behaviour of SF₆ has been studied by Sasaki et al. [10] up to 10 GPa by Raman spectroscopy who found two different crystalline phases, denoted as phase I and phase II. We recently explored the phase diagram of SF₆ by means of X-ray diffraction and micro-Raman spectroscopy up to 32 GPa and observed two additional phase transformations at 10 GPa and 19 GPa, respectively [11]. The SF₆ molecule was stable up to the highest applied pressure at ambient temperature.

CO is an example which showed that the reaction products at high pressures are not always crystalline but may be poorly crystalline or amorphous. Total-scattering techniques have been demonstrated to be a powerful tool for the determination of accurate structural parameters of crystalline as well as disordered, amorphous and nanocrystalline materials [12, 13] also at high pressures [14, 15]. The pair distribution function (PDF, $G(r)$) gives the probability of finding atoms separated by a distance r . $G(r)$ is experimentally obtained by a Fourier transformation of corrected and normalised powder diffraction data, $S(Q)$:

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q [S(Q) - 1] \sin(Qr) dQ \quad (1)$$

$\rho(r)$ is the microscopic pair density, ρ_0 is the average number density, $S(Q)$ is the total scattering structure function and Q is the magnitude of the scattering vector, which is given by $Q = 4\pi \sin \theta / \lambda$ with θ being the scattering angle and λ the wavelength of the radiation. Detailed information on the procedures can be found in Egami and Billinge [16].

In the current study, we explored the stability field of SF₆ at high pressures and high temperatures. The reaction products are analysed by X-ray diffraction, including pair distribution function analysis, and micro-Raman spectroscopy combined with atomistic model calculations.

2. Experimental details

A binary gas mixture of SF₆ and He with 10.4(2) vol% SF₆ was obtained from Praxair and loaded without further purification with the gas loading

system in Frankfurt. Boehler-Almax [17] type DACs with opening angles of 48° to 70° and culet sizes of $350\text{ }\mu\text{m}$ were employed. Tungsten gaskets with an initial thickness of $200\text{ }\mu\text{m}$ were preindented to $50\text{--}52\text{ }\mu\text{m}$ and holes of $133\text{--}140\text{ }\mu\text{m}$ were drilled with a laser lathe. The pressure was determined with the ruby fluorescence method [18, 19].

The laser heating experiments were performed in Frankfurt using a pulsed CO_2 laser ($\lambda = 10.6\text{ }\mu\text{m}$, 250 W) and at the Extreme Conditions Beamline P02.2 [20] (PETRA III, DESY, Hamburg) using a Yb fibre laser ($\lambda = 1070\text{ nm}$, 100 W). Two different samples containing the $\text{SF}_6\text{--He}$ mixture and glassy carbon, which was used as laser absorber (coupler), were heated at $11.3(3)\text{ GPa}$ and $10.0(2)\text{ GPa}$, respectively. KCl was used for thermal insulation. The temperature during laser heating was determined to be between $2000(100)\text{ K}$ and $2500(100)\text{ K}$ by fitting a Wien function to thermal emission spectra.

Raman spectra of the starting materials inside the DAC as well as the laser heating products inside the DAC at high pressures and recovered at ambient conditions after unloading the DAC were measured in Frankfurt with a Renishaw micro-Raman spectrometer (RM-1000) using a Nd:YAG laser ($\lambda = 532\text{ nm}$, 200 mW) and at the Extreme Conditions Beamline P02.2 using a green solid state laser ($\lambda = 532\text{ nm}$, 330 mW). The positions of the Raman bands were determined by single-peak fits using Pseudo-Voigt functions. The fits were performed with the program *KUPLOT* [21].

Synchrotron X-ray diffraction experiments before and after laser heating were performed at P02.2. We used radiation with energies around 42.8 keV ($\lambda = 0.290\text{ \AA}$). The beam was focused to approximately $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ FWHM with Kirkpatrick-Baez mirrors or $9\text{ }\mu\text{m} \times 3\text{ }\mu\text{m}$ FWHM with a compound refractive lens system. Powder diffractograms were collected with a PerkinElmer XRD 1621 detector. The sample-detector distance was 400 mm. The data collection times varied between 10 s and 60 s. Diffraction patterns were measured at around 10 and 12 GPa before and after laser heating and at ambient conditions with open DACs.

The X-ray powder diffraction data were processed with the *Fit2D* [22] software. A CeO_2 standard was used for calibration. The diamond reflections were manually masked and excluded from the integration. Le Bail [23] and Rietveld [24, 25] refinements were performed with the programs *GSAS* [26] and *EXPGUI* [27]. The background was interpolated with a shifted Chebyshev function between manually defined points. Profile parameters (GW and LX, profile function 2), lattice parameters and a scaling factor

were refined. PDFs were obtained by a Fourier transform of the corrected and normalized patterns using standard procedures and those unique to area detectors implemented in the program *PDFgetX2* [28] which are described in Chupas et al. [29]. The powder diffractograms were terminated at a Q_{max} of $8 \text{ \AA}^{-1}$. PDF simulations were performed with the program *PDFgui* [30]. The atomic positions, unit cell parameters and isotropic displacement parameters ($u_{\text{iso}} = 0.02 \text{ \AA}^2$) were fixed and a scaling factor, Q_{damp} and δ_2 were refined.

3. Computational details

Structural models for the modelling of the laser heating products were obtained by density-functional-theory-based calculations [31] using the program *CASTEP* [32]. The geometries of the following structural models were optimised at different pressures: α -S₈, ϵ -S₆, S-II and CF₄-III. α -S₈ crystallises in space group *Fddd* with $Z = 16$; the atoms form discrete rings which are composed of 8 atoms [33]. ϵ -S₆ crystallises in space group *R $\bar{3}$* with $Z = 3$; the atoms form discrete rings which are composed of 6 atoms [34]. S-II crystallises in space group *P3₂21* with $Z = 9$; the atoms form helical chains [35]. For CF₄-III the model proposed by Shindo et al. [36] and Zhang et al. [37] with space group *P2₁/c* and $Z = 4$ was used.

The calculations for sulfur were performed with the “on-the-fly” pseudopotentials from the *CASTEP* database using a kinetic cut-off energy of 330 eV and Monkhorst-Pack grids [38], so that distances between k-points were $\leq 0.03 \text{ \AA}^{-1}$. Two approaches were employed: PBE-GGA [39] with the dispersion correction by Tkatchenko and Scheffler [40] and GGA with the Wu-Cohen [41] exchange correlation functional.

For the CF₄ calculation, norm-conserving pseudopotentials were used from the *CASTEP* database and the Wu-Cohen exchange correlation functional was employed. The kinetic cut-off energy was 940 eV, distances between sampling points were $\leq 0.037 \text{ \AA}^{-1}$ generated by a $4 \times 6 \times 4$ Monkhorst-Pack grid. Raman activities were calculated using density functional perturbation theory (DFPT) [42, 43]. The theoretical Raman frequencies were multiplied with a scaling factor of 1.03, as DFT-GGA calculations such as those performed here give too low frequencies [44].

4. Results

4.1. Agreement between model calculations and experiments

The reliability of the atomistic model calculations was established by comparing the lattice parameters with experimentally determined values. The cell parameters of all the DFT-optimised models are summarised in table 1. The values were consistent with experimental data reported earlier. For α -S₈ the discrepancies of the lattice parameters were between 1.5 % and 3 % compared to values reported by Rettig and Trotter [33] and Luo and Ruoff [45]. For S-II at 3 GPa, the discrepancies of the lattice parameters were between 0.7 % and 1.6 % with respect to experimental values of Crichton et al. [35]. The lattice parameters of CF₄-III were reproduced very well by the DFT calculation, the discrepancies were less than 0.7 %. From the good agreement with the available experimental data we expect to reasonably predict the high-pressure behaviour of these phases. The crystal structures of the DFT-optimised sulfur allotropes are presented in figure 1.

Table 1: Lattice parameters of the sulfur phases and CF₄-III at different pressures and temperatures from DFT, experiment and literature.

model	p/GPa	T/K	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$	$V/\text{\AA}^3$
α -S ₈ , exp. [†]	0	300	10.457(6)	12.785(4)	24.655(7)	–	3296(2)
α -S ₈ , exp. [33]	0	298	10.4646(1)	12.8660(1)	24.4860(3)	–	3296.73
α -S ₈ , exp. [45]	0	300	10.45	12.80	24.64	–	3295.85
α -S ₈ [*]	0	–	10.714	13.169	25.173	–	3551.7
α -S ₈ ^{**}	0	–	10.751	13.113	24.264	–	3420.7
α -S ₈ [*]	11	–	9.0666	11.4200	22.3889	–	2318.2
α -S ₈ ^{**}	11	–	8.9154	11.2600	22.1676	–	2225.3
ϵ -S ₆ [*]	11	–	9.8568	–	3.6261	–	305.1
S-II [*]	3	–	7.2019	–	4.3356	–	194.7
S-II, exp. [35]	3	673	7.0897	–	4.3024	–	187.3
S-II [*]	11	–	6.5549	–	4.2126	–	156.8
CF ₄ -III, exp. [36]	6.2	300	6.776	4.423	6.818	102.97	199.1
CF ₄ -III ^{**}	6.2	–	6.8163	4.4553	6.8603	102.78	203.2
CF ₄ -III, exp. [‡]	11.6(2)	300	6.51(1)	4.332(6)	6.63(1)	102.1(1)	182.9(4)
CF ₄ -III ^{**}	11	–	6.5589	4.3164	6.5972	102.44	182.4

^{*}this study, GGA-PBE+TS; ^{**}this study, GGA-WC

[†]this study, Le Bail refinement; [‡]this study, Rietveld refinement

4.2. Laser heating SF₆ and glassy carbon

Laser heating colourless SF₆ in a diamond anvil cell (DAC) at 10 GPa without a laser absorber (coupler) or with a sapphire plate as absorber did

Figure 1: Crystal structures of the DFT-optimised sulfur allotropes S-II shown along c and along a , α -S₈ along a and ϵ -S₆ along c .

not lead to a significant increase in temperature and a chemical reaction. The use of glassy carbon as laser absorber resulted in a reaction. Pictures of the samples of two different laser heating experiments (referred to as #9 and #12) are presented in figures 2 and 3. One experiment was performed with a single glassy carbon sphere (#9, figure 2) and another one with several spheres (#12, figure 3). The temperatures during laser heating were determined to be 2000(100) K to 2500(100) K. In both cases a chemical reaction occurred, since the black spheres were no longer visible after the heating, but instead dark red, orange and yellow coloured phases were present. During pressure release, the colours changed from dark red and orange to light orange and yellow, respectively. At ambient pressure the samples were pale yellow to colourless.

Figure 2: SF₆ and a glassy carbon sphere before and after laser heating and during decompression.

Figure 3: SF_6 and glassy carbon before and after laser heating and during decompression.

4.3. Powder X-ray diffraction

Figure 4 shows 2D diffraction images before and after laser heating of the sample presented in figure 2 (as the amount of sample was very small in experiment #9, the diffraction experiments were performed with the sample of experiment #12 only). After heating, the broad textured reflections of SF_6 disappeared and sharp reflections of the laser heating products were visible.

Figure 4: 2D diffraction images before (left) and after (right) laser heating SF_6 and glassy carbon at 10.0(2) GPa.

Figure 5 depicts integrated diffraction data of the laser heating products of the sample presented in figure 3. A systematic data collection revealed that the sample contained crystalline products in the outer part and amorphous products in the inner part (figure 5).

4.3.1. Pair distribution function analysis of the amorphous reaction products

The diffraction pattern of the amorphous product(s) was extracted by excluding reflections of the crystalline product(s) from the integration and by manually removing reflections from the integrated data. Sharp reflections

Figure 5: Left: X-ray diffraction patterns of the amorphous (red) and crystalline (blue) laser heating products of SF_6 and glassy carbon. Right: Area of the sample which contained the amorphous and crystalline reaction products. The arrows mark the positions where the diffraction patterns were collected.

were manually removed by interpolating spline functions between points that were chosen to be the beginning and end of a reflection. As it was difficult to distinguish between the particular reflection and the background at high Q values, the data was terminated at a Q_{max} of $8 \text{ \AA}^{-1}$. A PDF was obtained (figure 6, top) which showed the first structural peak at $2.0(1) \text{ \AA}$. This value is consistent with known bond lengths of S-S bonds: the S-S bond lengths in S-II at 3 GPa and 400 K are $2.070(4) \text{ \AA}$ and $2.096(7) \text{ \AA}$ [35]. In the DFT-optimised sulfur allotropes introduced in section 3, the S-S bond lengths vary between $2.02 \text{ \AA}$ and $2.07 \text{ \AA}$. C-F and S-F bonds have lengths of around $1.3 \text{ \AA}$ [46] and $1.6 \text{ \AA}$ [47]. If there was a significant contribution of C-F or S-F bonds, we expect that the position of the first peak would be well below $2 \text{ \AA}$.

In order to obtain information on the local atomic structure of the amorphous product, PDFs of the different DFT-optimised sulfur allotropes were simulated. These PDFs are also shown in figure 6. The simulated PDF of crystalline helical S-II is very similar to the experimental PDF of the amorphous reaction product.

The similarity of the simulated PDF of helical S-II to the experimental

Figure 6: Experimental PDF of the amorphous reaction product at 11.6(2) GPa (top, dotted line) and simulated PDFs of DFT-optimised structural models of different sulfur allotropes (bottom, solid lines).

PDF up to ≈ 5 Å was confirmed by PDF simulations where experimental parameters such as scaling factor, dampening envelope parameter Q_{damp} and peak sharpening parameter δ_2 were refined. The results of the simulations are presented in figure 7 and summarised in table 2 which shows all the refined parameters. The agreement between the experimental PDF and the simulated PDF of helical S-II is good. This is also reflected in the R_w values of the refinements (table 2). Due to the limited quality of the experimental PDF we cannot rule out the presence of S_8 and S_6 . However, we conclude that the majority of the amorphous reaction product is sulfur which contains helical chains.

Table 2: Results of the PDF simulations of the amorphous reaction product (fit range: 1 to 10 Å).

model	scaling factor	Q_{damp}	δ_2	$R_w/\%$
S-II*	1.253(5)	0.276(1)	1.47(4)	37.7
α - S_8 *	1.248(6)	0.315(1)	2.14(4)	48.4
ϵ - S_6 *	1.358(6)	0.327(1)	2.06(3)	54.0

*this study, GGA-PBE+TS, 11 GPa

Figure 7: PDF simulations of the amorphous reaction product. The experimental PDF is shown as dotted line (blue), the simulated PDF is shown with a solid line (red) and the difference curve is below (green).

4.3.2. Analysis of the crystalline reaction products

The diffraction patterns of samples recovered at ambient conditions showed only crystalline phases. The Le Bail refinement of the diffraction pattern collected of a recovered sample at ambient pressure is presented in figure 8. All reflections could be described by the phases KCl (thermal insulator), W (gas-ket) and α -S₈. The refined lattice parameters of α -S₈ are given in table 1. They are in very good agreement with lattice parameters reported earlier [33, 45].

Figure 8: Le Bail refinement of the reaction product recovered at ambient conditions (blue crosses: observed data, red line: simulated pattern, green line: difference curve, tic marks: calculated reflection positions).

The crystalline reaction products at 11.6(2) GPa could not be identified unambiguously due to the many overlapping reflections. Since at ambient conditions the diffraction pattern showed only sulfur, further reaction products were assumed to be volatile compounds with the general chemical formula C_xF_y . Figure 9 depicts the comparison of the background subtracted diffraction pattern of the crystalline reaction products at 11.6(2) GPa with the simulated powder diffraction pattern of CF₄-III. The simulated pattern is the result of a Rietveld refinement where the DFT-optimised CF₄-III was used as starting model and a scaling factor, the lattice parameters and profile parameters were refined. The reflections of CF₄ are reproduced very well. This indicates that CF₄ might be a reaction product. The indexing of the

remaining reflections was not successful.

Figure 9: Top: Background subtracted diffraction pattern of the crystalline reaction product at 11.6(2) GPa (blue) and simulated diffraction pattern and reflection positions (tic marks) of $\text{CF}_4\text{-III}$ (red). The simulated pattern is the result of a Rietveld refinement. Bottom: DFT-optimised crystal structure of $\text{CF}_4\text{-III}$ at 11 GPa (C: grey, F: green, view along b).

4.4. Raman spectroscopy

Figure 10 presents Raman spectra of SF_6 and glassy carbon before and after laser heating at 11.3(3) GPa measured at different positions on the sample (due to the small amount of sample in exp. #9, all the Raman measurements, except those of the recovered samples, correspond to exp. #12). The coloured areas of the sample did not show bands characteristic

for SF₆. The Raman spectra of the inner dark and yellow part of the sample consisted of very broad bands. The most intense of these bands was located at around 460 cm⁻¹. This position is characteristic for stretching modes of many sulfur allotropes [48]. The broad bands can therefore be correlated with amorphous sulfur. The Raman spectrum which was measured in the outer red part of the sample consisted of broad bands as well as sharper bands at 600 cm⁻¹ to 950 cm⁻¹ where no sulfur modes are expected. This result is consistent with the X-ray diffraction data which showed amorphous sulfur in the inner part and other crystalline products in the outer part of the sample. Figure 11 depicts the Raman spectra of the laser heating products during decompression to ambient pressure. The FWHM of the Raman bands decreased with decreasing pressure revealing the fine structure of the bands. In addition to the sulfur band at around 460 cm⁻¹, bands at higher wavenumbers of up to 550 cm⁻¹ became observable. Eckert et al. [48] have studied the phase transformations of sulfur at high pressures. Most sulfur allotropes do not have bands at 500 cm⁻¹ to 600 cm⁻¹. However, a sulfur allotrope named p-S has bands in this region [48]. Degtyareva et al. [49] have shown that p-S corresponds to helical S-II or is at least structurally closely related to it. Thus, the PDF simulations as well as the Raman spectra indicate that the amorphous laser heating product is sulfur consisting of helical chains. After opening the DAC the Raman spectrum changed with time and within a few minutes we observed that S-II transformed to S₈.

Some of the sharp bands in the Raman spectra of the reaction products at 11.6(2) GPa can be assigned to CF₄-III (figure 12). The identification of the other bands was not successful. Figure 12 shows the Raman spectrum of the laser heating products at 11.6(2) GPa, experimental Raman spectra of p-S and CF₄ by Orgzall and Lorenz [50] and Shindo et al. [36], respectively. Moreover, the theoretical Raman spectrum of CF₄-III at 11.6 GPa is presented. The DFT simulations allow a detailed analysis of the Raman spectrum of CF₄-III. A symmetry analysis gives the total representation of CF₄-III as

$$\Gamma = \underbrace{A_u + 2B_u}_{\text{acoustic}} + \underbrace{14A_u + 13B_u + 15A_g + 15B_g}_{\text{optic}}$$

where the modes in the latter two groups are Raman active. Hence, there are in total 30 Raman active modes. Of these 8–9 can be observed unambiguously [51, 36]. A theoretical Raman spectrum of CF₄-III at 6.2 GPa is

Figure 10: Left: Raman spectra of SF_6 and glassy carbon at 11.3(3) GPa before and after heating. The arrow marks the approximate position where the G bands of graphite and glassy carbon are expected. The range around the diamond band was excluded. Right: Corresponding laser heated sample. The positions where the spectra were measured are denoted.

shown in figure 13, where it is compared to experimental data by Sasaki et al. [51]. The modes correspond to C–F₂ bending (ν_2), C–F₃ bending (ν_4), symmetric stretching (ν_1) and antisymmetric stretching (ν_3) [51]. The Raman frequencies of the experimental and theoretical data for CF₄-III at the different pressures are summarised in table 3. At 6.2 GPa, the maximum difference between theoretical and experimental frequencies was 4 %. At 11.6 GPa, the maximum difference between theory and experiment was 1.7 %. The positions of the theoretical frequencies were systematically underestimated at low frequencies and overestimated at high frequencies. The Raman spectra of Sasaki et al. [51] and Shindo et al. [36] in figures 12 and 13 are not plotted on a single scale, as the authors presented partial spectra only.

Raman spectra of the laser heating products recovered at ambient conditions are presented in figure 14. The observed Raman bands were characteristic for S_μ and α-S₈, respectively. S_μ is a sulfur allotrope which consists of helical chains [48] but it is unclear if the structure is similar to that of S-II or not. The reference spectra for these sulfur allotropes by Eckert et al. [48] are

Figure 11: Raman spectra of the laser heating products during decompression (the pressure decreases from bottom to top).

also shown in figure 14. The range of the reference spectra was limited, the bands at around 800 cm^{-1} to 950 cm^{-1} are overtones of the presented modes [52]. The laser heating product of the single glassy carbon sphere and SF_6 did not show any bands which are characteristic for carbon allotropes. The laser heating product of the experiment with several glassy carbon spheres showed weak bands in the range of 1200 cm^{-1} to 1600 cm^{-1} where vibrations of sp^2 and sp^3 hybridised carbon are expected. These bands could not be explained with glassy carbon and are probably caused by a different amorphous carbon allotrope.

Figure 12: Raman spectrum of the laser heating product of SF_6 and glassy carbon at 11.6(2) GPa (blue) compared to theoretical data at 11.6 GPa (red) and experimental data for CF_4 at 12.1 GPa by Shindo *et al.* [36] (black) and for p-S at 5 GPa by Orgzall and Lorenz [50] (grey). The spectra of Shindo *et al.* [36] are not plotted on a single scale. The energies of the theoretical data are scaled by a factor of 1.03.

Figure 13: Theoretical Raman spectrum of $\text{CF}_4\text{-III}$ at 6.2 GPa (blue) and experimental data at 6.3 GPa by Sasaki *et al.* [51] (black). The four spectra of Sasaki *et al.* [51] are not plotted on a single scale. The energies of the theoretical data are scaled by a factor of 1.03.

Table 3: Raman frequencies of CF_4 from theoretical and experimental data. The energies of the theoretical data are scaled by a factor of 1.03.

ν/cm^{-1}				
6.2 GPa		6.3 GPa	11.6 GPa	11.6(2) GPa
DFT		exp.	DFT	exp.
this study	Sasaki et al. [51]		this study	this study
429.53	442.8		439.39	n.o.
435.77	450.1		445.79	n.o.
443.21	460.8		459.73	n.o.
444.23	n.o.		463.5	n.o.
627.86	n.o.		633.31	n.o.
628.87	642.0		635.58	644.0(1)
631.10	n.o.		640.56	n.o.
632.06	646.0		640.94	651.63(6)
633.06	647.9		642.24	n.o.
942.76	931.3		957.61	943.70(2)
1244.42	1231.9		1252.24	n.o.
1266.47	1248.5		1277.62	n.o.
1269.22	n.o.		1281.22	n.o.
1284.48	n.o.		1297.84	n.o.
1349.45	n.o.		1364.70	n.o.
1373.93	n.o.		1394.66	n.o.

n.o.: not observable

Table 4: Raman frequencies of the recovered laser heating products at ambient conditions compared to data given by Eckert et al. [48].

ν/cm^{-1}			
exp. #9	exp. S_μ	exp. #12	exp. S_8
this study	Eckert et al. [48]	this study	Eckert et al. [48]
		153.03(2)	150
		193.4(5)	n.o.
217.57(2)	220	213.29(5)	n.o.
259.96(3)	264	219.61(3)	219
273.09(2)	274	240.8(4)	n.o.
416.05(3)	420	247.9(5)	246
423.75(2)	n.o.	431.0(6)	n.o.
454.14(4)	456	440.1(3)	433
462.5(3)	n.o.	472.94(1)	470

n.o.: not observable

Figure 14: Raman spectra of the recovered laser heating products of two different laser heating experiments. The black line depicts data for S_μ and $\alpha\text{-S}_8$ from Eckert *et al.* [48].

5. Discussion and Conclusions

The laser heating products of SF_6 and glassy carbon were analysed using X-ray diffraction, including pair distribution function analysis, and Raman spectroscopy. Both methods indicate that laser heating at 10 GPa to 11 GPa and 2000 K to 2500 K resulted in the formation of elemental sulfur and probably CF_4 -III and other volatile compounds with the general chemical formula C_xF_y . Degtyareva et al. [49] reported on the high pressure and high temperature phases of sulfur. In the pressure range of this study, there are two possible sulfur phases at high temperatures, S-II (helical) and S-VI (S_6 molecules) [49]. The molecular S_6 phase has been observed by heating sulfur at 7 GPa to 11 GPa and 650 K to 1000 K [53, 49]. The helical S-II has been reported to form by heating sulfur above 1.5 GPa close to the melting temperature [35, 54, 55]. Both phases are quenchable to ambient temperature at high pressure. The PDF analysis of the amorphous reaction product at high pressures clearly showed that the major phase is helical sulphur. Hence, the pressure and temperature conditions of the present experiments favoured the formation of helical sulfur chains instead of S_6 molecules. The recovered samples in this study showed the thermodynamically stable α - S_8 phase as well as S_μ . S_μ is known to be metastable at ambient conditions and the transformation to α - S_8 can be very slow [56].

The existence of elemental sulfur can additionally be confirmed by the colour change of the product during decompression. The colour changed from dark-red at high pressures to pale yellow and colourless at ambient pressure. Chen and Wang [57] have observed that yellow sulfur turns red at 5 GPa to 6.5 GPa and black at 10 GPa to 12 GPa.

The phase diagram of CF_4 has been studied by several groups [51, 58, 59, 36, 37]. Lorenzana et al. [59] state that the stable phase up to at least 16 GPa is phase III. This has been confirmed by atomistic model calculations which found that the transition pressure of phase III to phase IV is 22 GPa [37]. The analysis of the present data was performed with phase III, which is described in section 3. Hence, the existence of CF_4 -III in the pressure range of the present experiments is in accordance with previous results and an independent confirmation that CF_4 -III is at least metastable at 11.6(2) GPa and ambient temperature.

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