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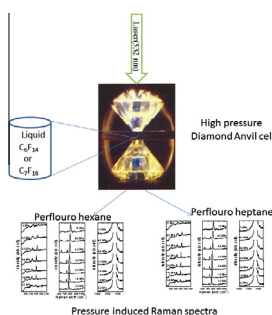
## Comparative high pressure Raman studies on perfluorohexane and perfluoroheptane <sup>☆</sup>

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### HIGHLIGHTS

- High pressure Raman spectroscopic studies on perfluorohexane and perfluoroheptane have been demonstrated.
- Pressure induced phase transitions have been indicated using  $\omega$ ,  $d\omega/dP$  order parameters.
- Solid I transition is observed in perfluoroheptane.
- Pressure induced behavior of mid-chain perfluorocarbon is different from mid-chain hydrocarbon.
- High pressure Raman studies on mid-chain perfluorocarbon till 12 GPa have been done for the first time.

### GRAPHICAL ABSTRACT



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### ABSTRACT

High pressure Raman spectroscopic studies on perfluorohexane and perfluoroheptane have performed up to 12 GPa. Perfluorohexane under goes two pressure induced transitions: (1) liquid–solid transition at 1.6 GPa and (2) solid–solid transition at 8.2 GPa. On the contrary, perfluoroheptane under goes three phase transitions, they are as follows: (1) liquid–solid transition at 1.3 GPa, (2) intermediate solid I transition at 3 GPa, (3) solid II transition at 7 GPa. The change in slope ( $d\omega/dP$ ) shows that the solid I transition at 3.0 GPa could be the conversion of mid-gauche defect into trans conformers for perfluoroheptane. The pressure induced Raman spectra and the behavior of individual band with pressure shows that the solid phase comprises more than one conformer beyond crystallization. The intensity ratio for both the compounds shows that the high pressure phase beyond 8.2 and 7.0 GPa tends to have close packing with distorted all-trans conformers.

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### Introduction

Recently, the interesting topic which draws every one's attention is the molecular orientation of simple hydrocarbons and perfluorocarbons at different high pressure phases. Perfluorocarbons have

molecular structure analogous to simple hydrocarbons where all the hydrogen atoms are replaced by fluorine atoms [1]. The industrial use is mainly linked to the electronic and computer industry [2–6]. The bonding nature is important for poly perfluoroethane to act as lubricant between magnetic hard disks and heads. Further perfluorocarbons have variety of potential applications in computer industry as lubricant, binary and ternary mixtures of liquid thin films and obtaining plastic crystals from molecular solids and so on [7–9]. So far, the number of investigations on

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perfluorocarbons is very less. So it will be interesting to investigate their molecular nature in detail. Temperature dependent vibrational behavior of perfluorocarbons has been studied by Rey-Lafon and co-workers [10,11]. Subjecting various types of matter to external pressure and utilizing Raman spectroscopic technique as the diagnostic tool, one can obtain the valuable information like intermolecular interaction, phase transition and structural changes. The existence of solid–solid transition in short chain and long chain perfluorocarbons under temperature has been reported earlier [12–15]. Though most of the physical and chemical properties of alkanes and perfluoroalkanes are same [16,17], their conformational properties are more complex due to their helical nature. So it is necessary to investigate the conformational characteristics and phase behavior of perfluorocarbons with pressure at different physical states. Due to this reason, we have carried out a comparative high pressure Raman studies on medium chain perfluorohexane and perfluoroheptane till 12 GPa. We found (1) liquid–solid transition at 1.6 GPa, (2) Solid I transition at 8.2 GPa for perfluorohexane. Further for perfluoroheptane, we have observed (1) liquid–solid transition at 1.3 GPa, (2) Intermediate solid I transition at 3.0 GPa, (3) solid II transition at 7.0 GPa. Pressure induced Solid–solid transitions in these perfluorocarbons has been observed for the first time. The conformational and the phase behavior of these perfluorocarbons at different high pressure phases have been discussed below.

### Experimental details

We have used gasketed Mao–Bell diamond anvil cell [18] (DAC) to obtain high pressure in this experiment. The spectroscopic grade perfluorohexane and per-fluoroheptane has obtained from Sigma Aldrich and has been used without further purification. This high pressure diamond anvil cell has two, fluorescence less type II diamonds with 500  $\mu\text{m}$  diameters. Perfluorocarbons were loaded in the gasketed diamond anvil cell along with <20  $\mu\text{m}$  ruby chip as a pressure sensor. The pressure was calibrated by ruby  $R_1$  line fluorescence method [19] with the accuracy of about  $\pm 1$  GPa. The backscattering geometry has been setup through an epi-illuminated, stage less, wall mounted microscope (Nikon, Japan). The solid state diode pumped Nd – YAG (SUWTECH, China)  $\approx 30$  mW lasers with excitation wavelength 532 nm has been focused on to the sample through the backscattering microscope set up [20]. The 20 $\times$  microscope objective having numerical aperture 0.35 have been used to focus the incident light on to the sample as well as to collect the Raman scattered light through 100  $\mu\text{m}$  single core optical fiber. The backscattering geometry has been obtained using dichroic beam splitter (6600 DCLP Chroma Technology Corp, USA.) which is kept at an angle 45 $^\circ$  between incident and scattered optical path. The scattered light passed through an edge filter (Semrock, UK) which is kept before optical fiber to cut the Raleigh line sharply. The Raman spectra were recorded using Jobin Yvon Triax 550 and a liquid N<sub>2</sub> cooled CCD detector (Horiba, USA). A digital camera (Nikon Coolpix 5400, Nikon, Japan) mounted on top of microscope has used to obtain the image of the laser spot and optical fiber at the same optical path. Because of tight focus, each resolved spectra have been recorded with 60 second from the sample. With an aid of origin software, one can obtain the valuable information like peak position, peak width, and the intensity of the Raman spectra using lorentzian fit.

### Results

Though some of the perfluorocarbon's properties are similar to simple hydrocarbons, the structure is little bit different from hydrocarbons [21]. Fig. 1(i and ii) shows the difference in

molecular structure of hexane and perfluorohexane. So it is clear that the perfluorocarbons are adopting the helical structure. This is due to greater van der Waals radius of fluorine atom compared to hydrogen atom in alkanes. Because of the smaller van der Waals radius of hydrogen atom in alkanes, they won't be able to touch each other. But in the case of perfluorocarbon, the atoms which are attached to the carbon back bone appeared to be over crowded due to greater van der Waals radius of fluorine atom [22]. To overcome this problem, the molecules adjust themselves with the rotation around the chain bonds to make distance between the fluorine atoms. So perfluorocarbons are helical in nature. Due to this reason, the back bone dihedral angles for the trans conformation are shifted by about 17 $^\circ$  from the true trans angle due to repulsive interaction of C–F's high polar nature [23]. The pressure induced behavior of medium chain perfluorohexane and perfluoroheptane has performed till 12 GPa in order to know about the structure of rotational isomers at different physical states.

Figs. 2 and 3 shows the Raman spectra in the spectral region (100–1500  $\text{cm}^{-1}$ ) of perfluorohexane and perfluoroheptane at ambient conditions and at high pressures. The Rayleigh frequency cut off for edge filter is around 100  $\text{cm}^{-1}$  and further use of dichroic mirror for back scattering geometry made us unable to get the low frequency modes below 100  $\text{cm}^{-1}$ . The presence of first order diamond peak at 1300  $\text{cm}^{-1}$  suppresses the weak Raman signal at that region.

The individual Raman mode behavior of perfluorohexane and perfluoroheptane with high pressures has been plotted in the Figs. 4–8. The Raman modes due to different kinds of vibrations are classified into (1) Longitudinal Acoustic Mode (LAM), (2) CF<sub>2</sub> Wagging, Twisting and Rocking region (275–350  $\text{cm}^{-1}$ ), (3) CF<sub>2</sub> and CF<sub>3</sub> Bending and Rocking region (350–620  $\text{cm}^{-1}$ ), (4) CF<sub>2</sub> and CF<sub>3</sub> Stretching region (700–1300  $\text{cm}^{-1}$ ), (5) Skeletal C–C stretching region. The individual Raman mode frequencies, their pressure derivatives ( $d\omega/dP$ ) and the vibrational mode assignments with respective phase transition pressures have been tabulated in the Tables 1 and 2 for perfluorohexane and perfluoroheptane separately. The mode assignments have explained from the following refs [10,11,24–30]. To the best of our knowledge, there is no experimental high pressure Raman studies on perfluorohexane and perfluoroheptane till 12 GPa.

#### Longitudinal acoustic mode (LAM – C–C–C – angle bending)

It is well known that LAMs are related to the in-phase C–C–C bond angle expansion and contraction which is also known as accordion mode. Like *n*-alkanes, the property of this mode depends on the length of the chain [31,32]. The Rayleigh frequency cutoff is 100  $\text{cm}^{-1}$  for edge filter so it is difficult to get the low frequency modes below than that. This mode seems to be very weak at liquid phase which also consistent with our recent studies on alkanes [33,34]. The well resolved mode which is centered at 180  $\text{cm}^{-1}$  becomes sharper at 1.6 GPa for perfluorohexane. This could be due to the onset of crystallization of the liquid perfluorohexane. In the case of perfluoroheptane, this mode centered at 152  $\text{cm}^{-1}$  and is observed beyond 1.3 GPa. It is clear from our observation that the LAM shifts to lower frequency when the chain length increases. This evolution is characteristic of C–C–C angle bending mode [10,11,35]. This mode and its behavior with high pressure has shown in Figs. 2a, 3a and 4(i, ii) for perfluorohexane and perfluoroheptane respectively. This mode happens to be hardened with pressure but there is slight change in the slope of the frequency profile at 3.0 GPa for perfluoroheptane. This is the signature of solid–solid I transition at the pressure range. Upon further compression, this vibration ceases to exist beyond 8.2 GPa for perfluorohexane. The same is observed at 7.0 GPa for perfluoroheptane. This suggests another solid–solid transition. The

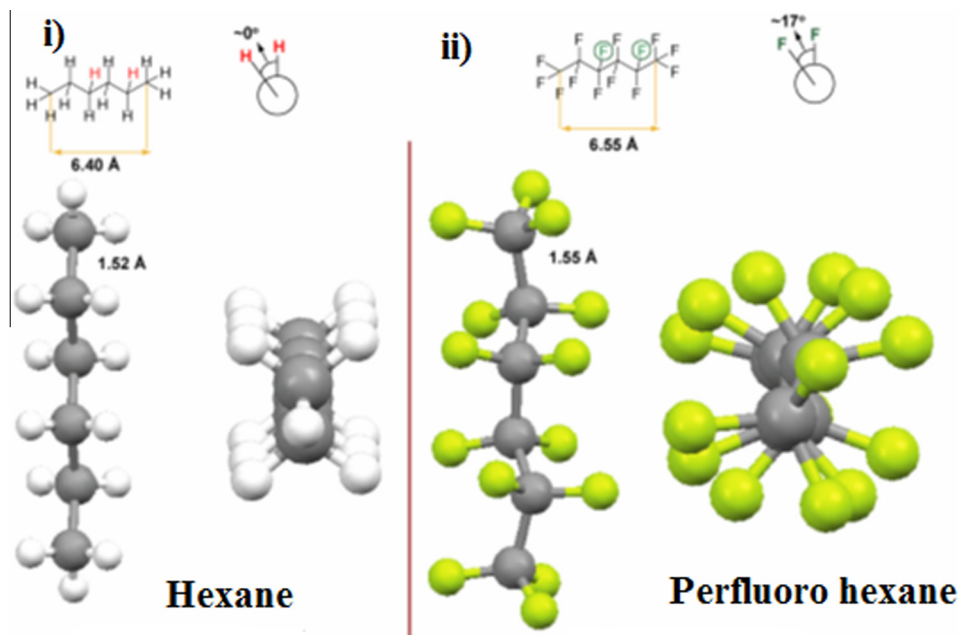


Fig. 1. The molecular structure of (i) Hexane, (ii) Perfluorohexane.

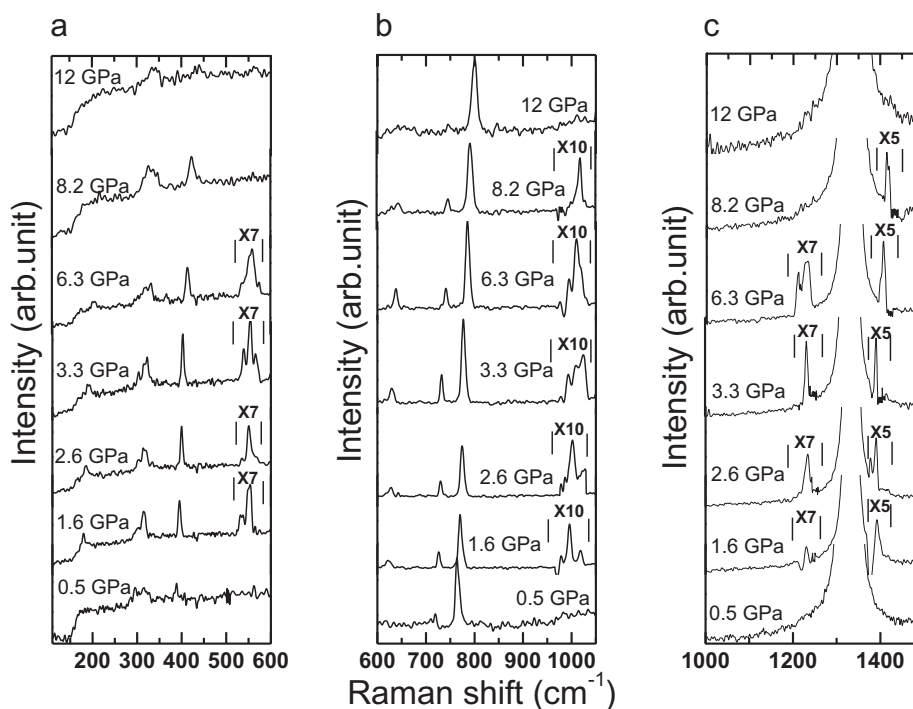


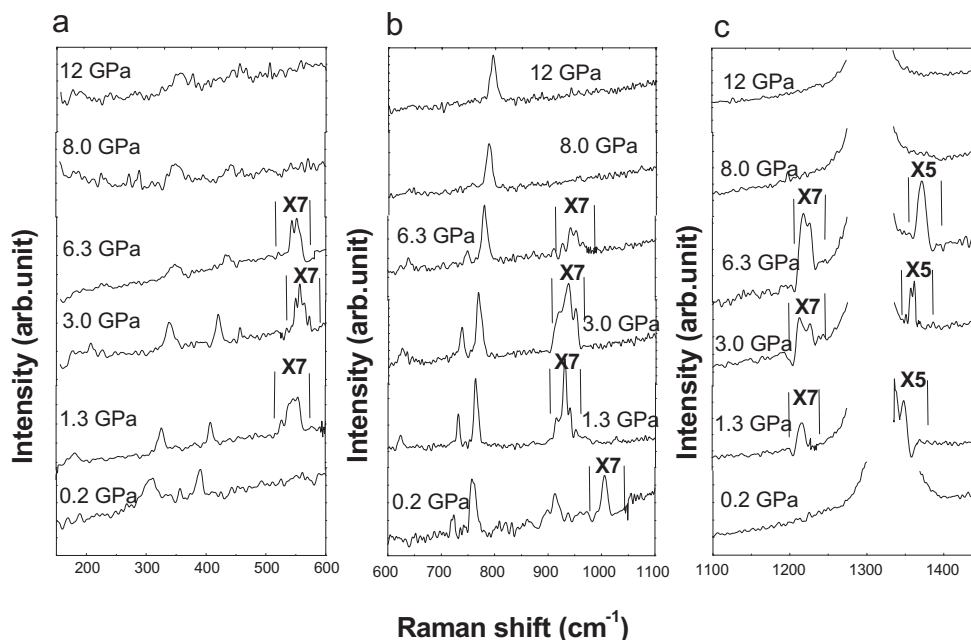
Fig. 2. Raman spectra of perfluorohexane recorded at ambient conditions and at high pressures. For clarity the spectra has been divided into three regions (a) 100–600  $\text{cm}^{-1}$ , (b) 600–1000  $\text{cm}^{-1}$  and (c) 1000–1500  $\text{cm}^{-1}$ . The 1200–1400  $\text{cm}^{-1}$  region is dominated by diamond first-order peak.

structural and conformational change with different physical states has been explained in the discussion section.

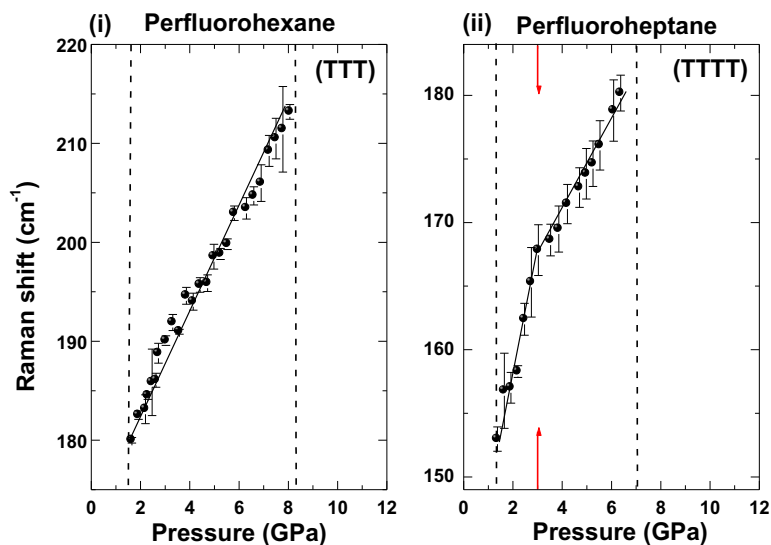
#### $\text{CF}_2$ wagging, twisting and rocking region (200–400 $\text{cm}^{-1}$ )

In the region 200–400  $\text{cm}^{-1}$ , the low frequency mode belongs to wagging motion and the high frequency mode belongs to twisting vibration in general. The existence of mode at 295  $\text{cm}^{-1}$  is responsible for  $\text{CF}_2$  wagging vibration and the modes at 312 and 327  $\text{cm}^{-1}$

are due to  $\text{CF}_2$  twisting vibration of the perfluorohexane. But in the case of perfluoroheptane, the two modes exist at 310 and 349  $\text{cm}^{-1}$  associated with  $\text{CF}_2$  Twisting and Rocking modes. These bands are attributed to the stable all-trans conformational isomer in the liquid phase. These modes are unresolved and featureless in the liquid phase. But beyond 1.6 GPa and 1.3 GPa for perfluorohexane and per-fluoroheptane, they became sharp and well resolved indicating the liquid–solid transition. This is due to periodic arrangement of molecules after the crystallization. More over the



**Fig. 3.** Raman Spectra of perfluoroheptane recorded at ambient conditions and at high pressures. For clarity the spectra has been divided into three regions (a) 100–600  $\text{cm}^{-1}$ , (b) 600–1100  $\text{cm}^{-1}$  and (c) 1100–1500  $\text{cm}^{-1}$ . The 1200–1400  $\text{cm}^{-1}$  region is dominated by diamond first-order peak.

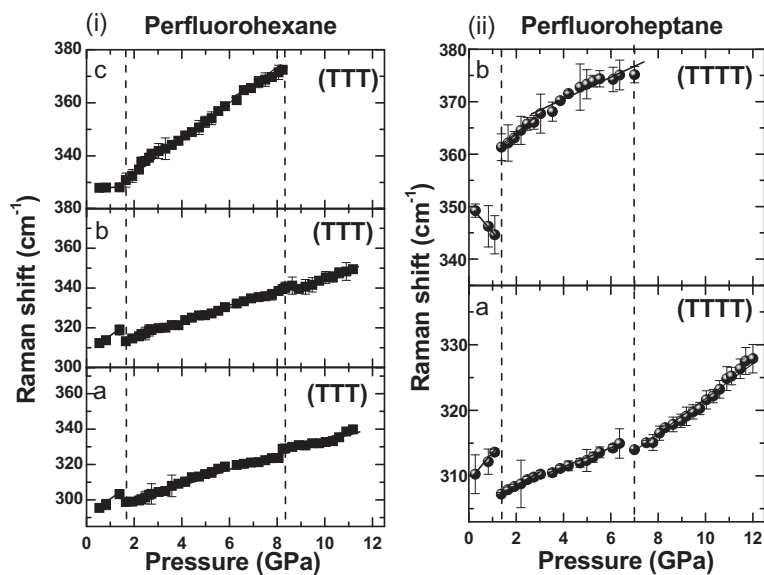


**Fig. 4.** (i) The perfluorohexane Raman mode associated with LAM as a function of Pressure. The solid lines through the data points are the linear fit to the data. The red color arrow shows the intermediate phase transition for perfluoroheptane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

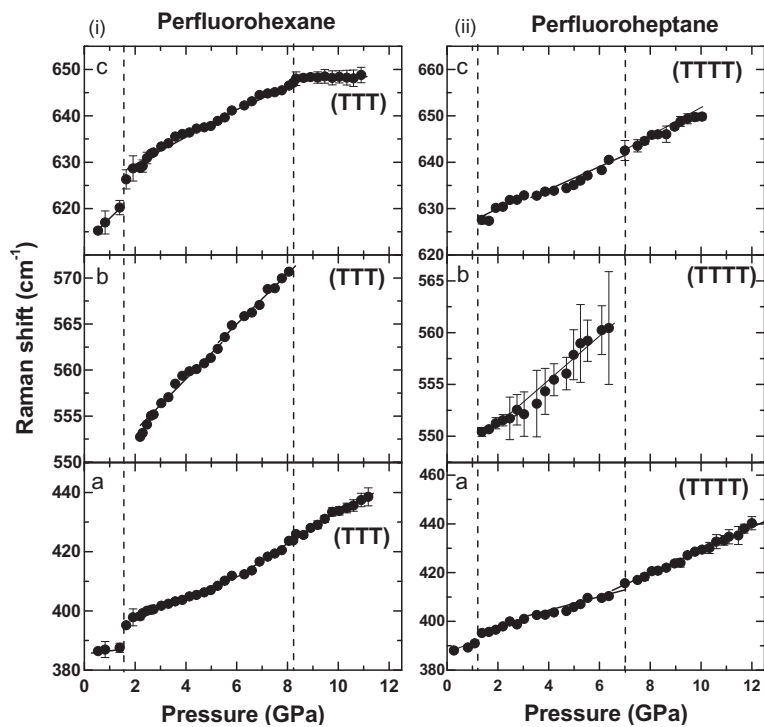
wagging, twisting and rocking modes of these two perfluorocarbons belongs to most stable all-trans isomers [10,11]. The response of these modes with increasing pressure are plotted in Fig. 5(i (a–c), ii (a–b)) for both perfluorocarbons. It is expected that these modes harden with pressure. There is no slope change at 3.0 GPa for perfluoroheptane (see Table 2). The only change is the intensity inversion of two  $\text{CF}_2$  twisting bands of two perfluorocarbons [10,35]. Further increase in pressure shows the finite change in pressure derivative. The disappearance of the twisting modes for both perfluoroalkanes indicates one more solid–solid transition around 8.2 GPa and 7.0 GPa respectively. The disappearance of the modes is clearly shown in the Figs. 2 and 3. The reason for the solid transitions will be discussed later.

#### $\text{CF}_2$ and $\text{CF}_3$ bending and rocking region (380–620 $\text{cm}^{-1}$ )

The Rocking mode is responsible for motion of the local molecular state and the conformational randomness. The state of the local molecular motion and the conformational randomness can be revealed by the bending mode vibrations at different high pressure phases. Like simple hydrocarbons, these modes are attributed to the chain packing and it reveals the order of chain termini at high pressure phase [36]. There are three modes in this region which belongs to more globular extended zigzag conformation. For perfluorohexane, the mode centered at 385, 552, 617  $\text{cm}^{-1}$  belongs to  $\text{CF}_2$  bending,  $\text{CF}_3$  Rocking and Asymmetric  $\text{CF}_3$  bending respectively. For perfluoroheptane, the characteristic bending



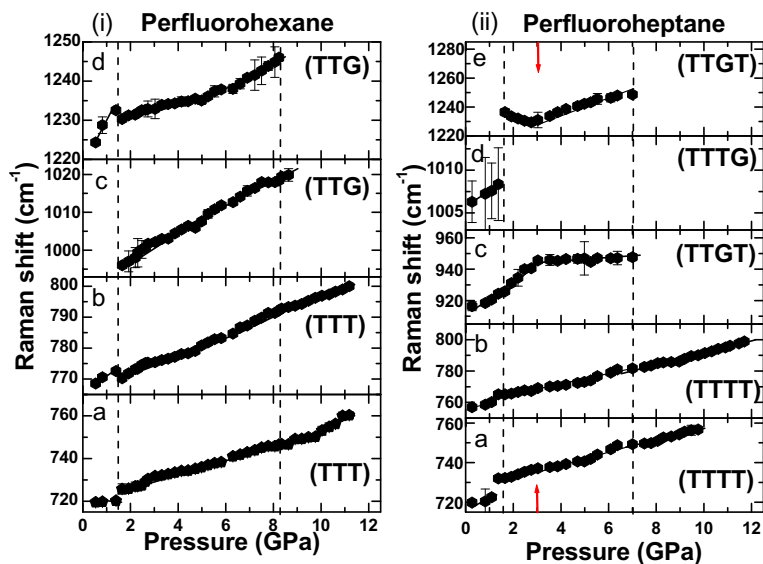
**Fig. 5.** (i) The perfluorohexane Raman modes associated with (a–c)  $\text{CF}_2$  Wagging and Twisting region as a function of pressure. (ii) The per fluoroheptane Raman modes associated with (a)  $\text{CF}_2$  Twisting and (b)  $\text{CF}_2$  Rocking region as a function of pressure. The solid lines through the data points are the linear fit to the data.



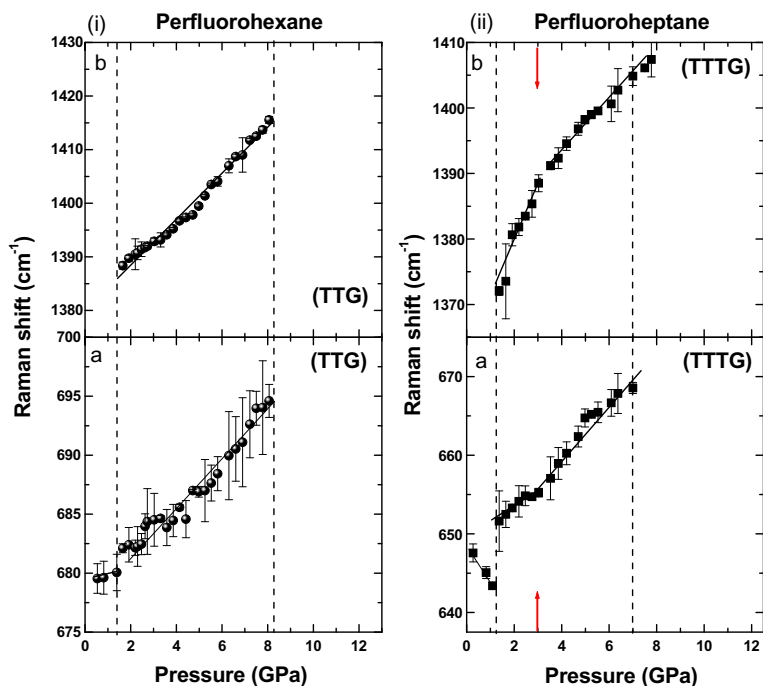
**Fig. 6.** (i) Perfluorohexane Raman modes associated with (a–c)  $\text{CF}_2$  and  $\text{CF}_3$  Bending and Rocking Region as a function of pressure, (ii) Per fluoroheptane Raman modes associated with (a–c)  $\text{CF}_2$  and  $\text{CF}_3$  Bending Region as a function of pressure. The solid lines are the linear fit to the data.

vibrations are  $388$ ,  $544$  and  $613\text{ cm}^{-1}$ . These modes are responsible for  $\text{CF}_2$  bending,  $\text{CF}_3$  bending and out of plane  $\text{CF}_3$  bending respectively. The behavior of these modes with pressure has plotted in Fig. 6 (i (a–c), ii (a–c)). The sudden jump in the frequency of  $385$  and  $617\text{ cm}^{-1}$  modes indicates that the crystallization of the perfluorohexane at  $1.6\text{ GPa}$ . The appearance of  $\text{CF}_3$  Rocking ( $552\text{ cm}^{-1}$ ) at  $1.6\text{ GPa}$  again represents the onset crystallization of perfluorohexane. The sudden appearance of two all-trans modes ( $545$ ,  $613\text{ cm}^{-1}$ ) at  $1.3\text{ GPa}$  indicates the crystalline nature of the perfluoroheptane. The change in slope for  $388\text{ cm}^{-1}$  mode at that

pressure range also suggests the same. The band at  $552\text{ cm}^{-1}$  assigned to trans linkage in the back bone [37]. Due to twisted nature of perfluorocarbons, all-trans conformers can be known as distorted all-trans conformers. There is no slope change for perfluoroheptane at  $3.0\text{ GPa}$ . What could be the reason for this? The reason will be presented below in detail. Further change in the slope ( $d\omega/dP$ ) and the disappearance of the  $552$ ,  $547\text{ cm}^{-1}$  rocking mode indicates another solid–solid transition at  $8.2$ ,  $7.0\text{ GPa}$  for both perfluorocarbons. This high pressure phase of perfluorocarbons will be discussed later.



**Fig. 7.** (i) a–d shows perfluorohexane's and (ii) (a–e) shows perfluoroheptane's CF<sub>2</sub> and CF<sub>3</sub> stretching Raman modes as a function of pressure. The solid lines are the linear fit to the data. The red color arrow shows the intermediate phase transition for perfluoroheptane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 8.** (i) a–b and (ii) a–b Skeletal C–C stretching modes of perfluorohexane and per fluoroheptane as a function of pressure respectively. The solid lines are the linear fit to the data. The red color arrow shows the intermediate phase transition for perfluoroheptane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### CF<sub>2</sub> and CF<sub>3</sub> stretching region (700–1250 cm<sup>-1</sup>)

These modes are responsible for different kinds of chain conformation and the chain packing [33,34]. There are four Raman bands for perfluorohexane which belongs to following region (a) 719 cm<sup>-1</sup> – symmetric CF<sub>2</sub> stretching (TTT), (b) 763 cm<sup>-1</sup> – symmetric CF<sub>3</sub> stretching (TTT), (c) 996, 1220 cm<sup>-1</sup> – CF<sub>3</sub> stretching and bending (TTG). But for perfluoroheptane, there are five modes observed in this region and they are as follows: (1) symmetric CF<sub>2</sub>

stretching (TTTT)-719 cm<sup>-1</sup>, (2) symmetric CF<sub>3</sub> stretching (TTTT)-755 cm<sup>-1</sup>, (3) CF<sub>3</sub> stretching and bending (TTGT)-916 cm<sup>-1</sup>, (4) CF<sub>3</sub> stretching and bending (TTTG)-1006 cm<sup>-1</sup>, (5) asymmetric CF<sub>2</sub> stretching (TTGT)-1236 cm<sup>-1</sup>. These modes are not well resolved in the liquid phase of perfluorocarbon. As per the Fig. 7(i) (a–d)), the appearance of 996 cm<sup>-1</sup> mode at 1.6 GPa indicates the liquid–solid transition. The sudden discontinuity in the slope also confirms the same. This reveals the fact that the solid phase contains more than one

**Table 1**

Frequency ( $\omega$ ) of the Raman modes of Perfluorohexane and its pressure derivative ( $d\omega/dP$ ) observed in the various phases are shown below respectively. Their mode assignments are also given based on Ref. [10,11,24–30].

Phase I (0.5 GPa)		Phase II (>1.6 GPa)		Phase III (>8.2 GPa)		Mode assignment
$\omega$ (cm <sup>-1</sup> )	$d\omega/dP$	$\omega$ (cm <sup>-1</sup> )	$d\omega/dP$	$\omega$ (cm <sup>-1</sup> )	$d\omega/dP$	
		180	5.2			LAM C–C–C angle bending
295	9.0	298	5.5	330	3.8	CF <sub>2</sub> Wagging (TTT)
313	7.7	312	3.7	339	4.4	CF <sub>2</sub> Twisting (TTT)
327	0.2	332	7.5			CF <sub>2</sub> Twisting (TTT)
385	1.3	395	3.4	425	4.5	CF <sub>2</sub> Bending (TTT)
		552	3.0			CF <sub>3</sub> Rocking (TTT)
615	5.8	627	2.7	647	0.1	Asymmetric CF <sub>3</sub> bending (TTT)
680	0.6	682	1.2			Chain Stretching (TTG)
719	0.8	726	2.7	747	4.8	Symmetric CF <sub>2</sub> stretching (TTT)
768	3.6	769	2.6	792	2.7	Symmetric CF <sub>3</sub> stretching (TTT)
		995	3.5			CF <sub>3</sub> stretching and bending (TTG)
1224	9.7	1230	1.5			Asymmetric CF <sub>2</sub> stretching (TTG)
1383	0.6	1388	3.8	1413	3.8	Symmetric C–C stretching (TTG)

conformer [10,11]. The intensity ratio  $I_{763}$  (TTT)/ $I_{993}$  (TTG) of the Raman bands shows the population of conformers at different physical states of perfluoroheptane [38].

This has been shown in Fig. 9(i). The disappearance of high frequency stretching modes 996, 1220 cm<sup>-1</sup> at 8.2 GPa pressure range indicates the structural transition with change in rotational isomers. These modes became sharp and having finite line width beyond 1.3 GPa in Fig. 7(ii) (a–e). This shows the crystalline state of the perfluoroheptane. The definite slope change of 719 cm<sup>-1</sup> and 755 cm<sup>-1</sup> modes, appearance (1236 cm<sup>-1</sup>) and disappearance (1006 cm<sup>-1</sup>) of the gauche modes after the solidification of perfluoroheptane confirms the presence of different conformers in the system. The qualitative intensity ratio  $I_{756}$  (TTTT)/ $I_{916}$  (TTGT) as shown in the Fig. 9(ii) also confirms the same. The drastic change in slope of these mid gauche (916, 1236 cm<sup>-1</sup>) modes at 3.0 GPa is the symbol for the structural transition in the system. But there is no slope change in all-trans modes at 3.0 GPa for perfluoroheptane. According to the mode behavior, the intermediate phase transition has not seen in perfluoroheptane. The reason will be discussed later. The persistence of all-trans modes (716, 754 cm<sup>-1</sup>) and disappearance of most of the gauche modes (917,

1236 cm<sup>-1</sup>) beyond 7.0 GPa suggest solid II transition in perfluoroheptane. This high pressure phase of both mid-chains perfluorocarbon will be explained in discussion section.

#### Skeletal C–C stretching region

Fig. 8(i (a–b)) shows the various C–C backbone stretching modes of perfluoroheptane and its behavior with pressure. Like simple alkanes, these modes are conformational sensitive in perfluoroalkanes. The modes at 678 and 1383 cm<sup>-1</sup> are attributed to the end gauche conformers (TTG). It is very clear that the sudden jump in the frequency and appearance of these modes at 1.6 GPa indicates the crystallization of perfluoroheptane. The disappearance of 678 and 1383 cm<sup>-1</sup> gauche mode indicate the structural transition at 8.2 GPa where the high pressure phase of perfluoroheptane prefers to have more globular extended zigzag conformers [38]. The definite slope change in this region has shown in Table 1 also confirm the same. The behavior of skeletal C–C stretching modes for perfluoroheptane centered at 647 cm<sup>-1</sup> (TTTG) and 1372 cm<sup>-1</sup> (TTTT) with pressure have shown in Fig. 8(ii (a–b)). The symbol for the solidification of perfluoroheptane beyond 1.3 GPa is discontinuity of the 647 cm<sup>-1</sup> mode and the appearance of the 1372 cm<sup>-1</sup> mode. This also supports that the solid perfluoroheptane contains different kinds of conformational isomers. The slope change near 3.0 GPa without spectral change (see Fig. 3) indicates possible phase transition in the system. Solid II transition at 7.0 GPa confirms by the disappearance of all gauche defect modes in the system. The explanation for this structural transition will be discussed below.

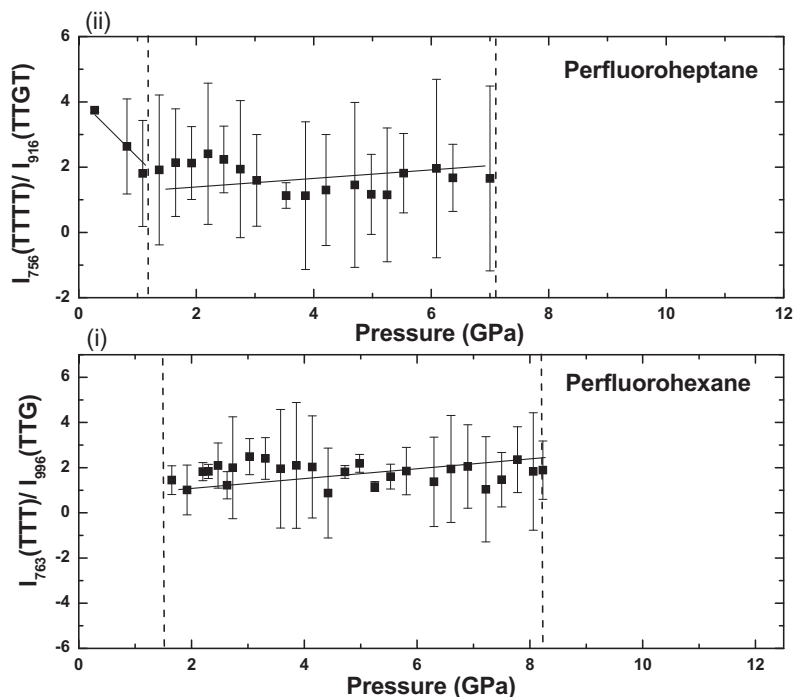
#### Discussions

The helicity of perfluorocarbons made the structural transition induced by thermodynamic variables, little different from simple hydrocarbons. The Raman spectrum of molecular solids is sensitive to the conformational rotational isomers. From the Figs. 2 and 3, the changes in the spectrum show the phase transitions with high pressure for both mid chains perfluorocarbons. It is well-known that the liquid phase of perfluoroheptane has all kinds of trans and gauche conformational isomers. These conformers exist randomly in the liquid phase. This has been shown by the unresolved broad Raman bands of perfluorocarbons in the liquid phase. The application of pressure causes two important phenomena in the molecular system [36], (1) increase in inter-molecular potential through van der Waals forces, (2) increase in intra-molecular potential through reduction in bond length. This could lead to the reduction in the volume of molecular system in the high

**Table 2**

Frequency ( $\omega$ ) of the Raman modes of Perfluoroheptane and its pressure derivative ( $d\omega/dP$ ) observed in the various phases are shown below respectively. Their mode assignments are also given based on Ref. [10,11,24–30].

Phase I (>0.2 GPa)		Phase II (>1.3 GPa)		Phase III (>3.0 GPa)		Phase IV (>7.0 GPa)		Mode assignment
$\omega$ (cm <sup>-1</sup> )	$d\omega/dP$	$\omega$ (cm <sup>-1</sup> )	$d\omega/dP$	$\omega$ (cm <sup>-1</sup> )	$d\omega/dP$	$\omega$ (cm <sup>-1</sup> )	$d\omega/dP$	
		152	7.9	167	3.8			LAM C–C–C angle bending
310	4.3	307	1.8	310	1.8	314	2.5	CF <sub>2</sub> Twisting (TTTT)
349	-5.5	361	3.7	367	3.7			CF <sub>2</sub> Rocking (TTTT)
388	3.5	396	3.5	401	3.5	415	4.7	CF <sub>2</sub> Bending (TTTT)
		550	1.4	552	1.4			CF <sub>3</sub> Bending (TTTT)
		627	3.3	631	3.3	641	2.6	Out of plane CF <sub>3</sub> Bending (TTTT)
647	-5.2	651	1.7	655	1.5			Chain Stretching (TTTG)-regular helix
719	3.3	733	3.4	736	3.4	750	2.9	Symmetric CF <sub>2</sub> stretching (TTTT)
755	4.0	765	2.4	769	2.4	782	3.8	Symmetric CF <sub>3</sub> stretching (TTTT)
914	8.8	927	13.0	946	0.5			CF <sub>3</sub> stretching and bending (TTGT)
1006	1.7							CF <sub>3</sub> stretching and bending (TTTG)
		1236	-5.3	1231	3.9			Asymmetric CF <sub>2</sub> stretching (TTGT)
		1372	10.0	1388	4.0			Symmetric C–C stretching (TTTT)



**Fig. 9.** (i) The intensity ratio  $I_{763}/I_{996}$  and (ii)  $I_{756}/I_{916}$  of *Trans* to *Gauche* conformational isomer of perfluorohexane and perfluoroheptane are plotted as a function of pressure. The solid lines are the linear fit to the data.

pressure phase. The behavior of all the Raman modes belongs to different conformers with high pressure has plotted in the Figs. 4–8.

#### Liquid–solid transitions at 1.6 GPa for perfluorohexane and at 1.3 GPa for perfluoroheptane

The slope change, the appearance of new modes belongs to different rotational isomers and the modes having finite band width at 1.6 GPa indicates the liquid–solid transition of perfluorohexane. Same way, 1.3 GPa is the solidification pressure for perfluoroheptane. The solidification pressure of perfluorocarbons is nearly same as that of the simple hydrocarbons. This has been reported earlier [34]. Due to intermolecular interaction, it is expected that the large change will occur on lattice, acoustic and librational modes with pressure. Appearance of LAM – C–C–C angle bending mode at the solidification state indicates the liquid–solid transition at 1.6 GPa, 1.3 GPa for perfluorohexane and perfluoroheptane respectively (see Fig. 4). The pressure induced slope change of  $\text{CF}_2$  wagging mode ( $295\text{ cm}^{-1}$ ) and  $\text{CF}_2$  twisting vibrations ( $312$  and  $327\text{ cm}^{-1}$ ) of the perfluorohexane at 1.6 GPa, the  $\text{CF}_2$  twisting mode ( $310\text{ cm}^{-1}$ ),  $\text{CF}_2$  rocking mode ( $349\text{ cm}^{-1}$ ) at 1.3 GPa for perfluoroheptane shows the liquid–solid transitions respectively (see Fig. 5). These bands are attributed to the stable all-*trans* conformational isomer in the liquid phase. The sudden jump in the frequency of  $\text{CF}_2$  bending ( $385\text{ cm}^{-1}$ ) and Asym  $\text{CF}_3$  bending ( $617\text{ cm}^{-1}$ ) modes indicates that the crystallization of the perfluorohexane at 1.6 GPa. The appearance of  $\text{CF}_3$  Rocking ( $552\text{ cm}^{-1}$ ) at 1.6 GPa again represents the onset crystallization of perfluorohexane. The sudden appearance of two all-*trans*  $\text{CF}_2$ ,  $\text{CF}_3$  modes ( $545$ ,  $617\text{ cm}^{-1}$ ) at 1.3 GPa indicates the crystalline nature of the perfluoroheptane (see Fig. 6). For perfluorohexane, the  $\text{CF}_2$ ,  $\text{CF}_3$  stretching ( $719$ ,  $763\text{ cm}^{-1}$ ) modes belongs to all *trans* conformation and other two  $\text{CF}_3$  stretching and bending modes ( $996$ ,  $1220\text{ cm}^{-1}$ ) belongs to TTG conformation respectively. The change in slope of  $763\text{ cm}^{-1}$ ,  $1220\text{ cm}^{-1}$  modes and the appearance of  $996\text{ cm}^{-1}$  at 1.6 GPa indicates liquid–solid transition. Further it also confirms that the solid

phase contains *gauche* defect with increase in all-*trans* conformation [10,11,35]. As in the case of perfluoroheptane, the discontinuity in the mode behavior ( $719\text{ cm}^{-1}$ -TTTT,  $756\text{ cm}^{-1}$ -TTTT,  $916\text{ cm}^{-1}$ -TTGT), disappearance ( $1006\text{ cm}^{-1}$ -TTTG) and appearance ( $1236\text{ cm}^{-1}$ -TTGT) of modes at 1.3 GPa also supports the same (see Fig. 7). The skeletal C–C stretching region is mainly sensitive to chain conformation. The discrete slope change and the appearance of the mode ( $678\text{ cm}^{-1}$ ) at 1.6 GPa indicate crystallinity of perfluorohexane. But in the case of perfluoroheptane, Both  $647$ ,  $1372\text{ cm}^{-1}$  C–C stretching modes possess end *gauche* conformation (TTTG). Mainly  $647\text{ cm}^{-1}$  belongs to regular helix chain stretching motion [39]. The appearance of  $1372\text{ cm}^{-1}$  and discontinuity in the  $647\text{ cm}^{-1}$  mode behavior at 1.3 GPa suggests the liquid–solid transition and also confirms that the solid phase contains more than one rotational isomers (see Fig. 8).

The intensity ratio  $I_{756}$  (TTTT)/ $I_{916}$  (TTGT) at 1.3 GPa for perfluoroheptane indicates the presence of more than one conformer after crystallization (see Fig. 9ii).

#### Intermediate solid I transition at 3 GPa for perfluoroheptane

LAM – C–C–C angle bending mode is expected to be harden with pressure. The subtle change in slope near 3.0 GPa represents the symbol for solid–solid transition for perfluoroheptane. This reveals the fact that the phase transition is related with conformational disorder (see Fig. 4ii indicated in red arrow). The intensity inversion of  $\text{CF}_2$  twisting and rocking modes occur at 3.0 GPa for perfluoroheptane. This has been proved by temperature dependent vibrational studies on perfluorocarbons [10,11,35]. But there is no slope change at 3.0 GPa for *trans* conformer modes indicate that the all-*trans* modes do not have any effect at this phase transition (see Fig. 5ii). Same way, There is no change in the pressure derivative of these bending modes ( $390$ ,  $550$ ,  $617\text{ cm}^{-1}$ ) at 3.0 GPa for perfluoroheptane. It shows that all-*trans* modes do not contribute for this phase transition (see Fig. 6ii). The drastic change in slope of these mid *gauche* ( $916$ ,  $1236\text{ cm}^{-1}$ )  $\text{CF}_2$ ,  $\text{CF}_3$  stretching modes at 3.0 GPa is the symbol for the structural transition in the system.



But there is no slope change in all-trans modes at 3.0 GPa for perfluoroheptane (see Fig. 7ii). This indicates the changes from mid gauche defect to trans conformers. There is no drastic change in the Raman spectra indicates that the molecular structure will be same as that of previous one. Because of the existence of more than one conformer, this transition could be conformational disorder. This has been previously reported by temperature dependent NMR and Raman studies on PTFE [37,39,40]. In the case of C–C stretching region, both 647, 1372  $\text{cm}^{-1}$  mode possess end gauche conformation (TTTG). The subtle slope change of these modes at 3.0 GPa could be the indirect contribution of these modes to the intermediate phase transition (see Fig. 8ii). This could be related to chain length of mid-chain perfluoroalkanes. The perfluorohexane has end-gauche defect where perfluoroheptane has mid-gauche and end-gauche due to increase in one carbon atom. Once the chain length increases, the number of solid–solid transition will be also increases due to the kinds of gauche defect present in the system. This transition is different from alkanes. This could be related to the rigid nature as well as the energy difference between gauche and trans states of the perfluoroalkanes. The energy difference between gauche and trans states are larger for perfluorocarbons. Perfluorohexane do not have a remarkable change for the intermediate phase transitions.

#### *Solid II transition at 8.2 GPa for perfluorohexane and 7 GPa for perfluoroheptane*

Further application of pressure, this LAM-C–C angle bending mode ceases to exist beyond 8.2, 7.0 GPa for both mid chain perfluoroalkanes indicates another solid–solid transition (see Fig. 4). This could mean that the execution of angle bending vibration will be difficult due to volume reduction with high pressure. But it is interesting that the  $\text{CF}_2$  wagging mode (295  $\text{cm}^{-1}$ ) for perfluorohexane and  $\text{CF}_2$  twisting mode (310  $\text{cm}^{-1}$ ) for perfluoroheptane still persist till 12 GPa indicates the high pressure phase contains only all-trans conformers which is true for mid-chain alkanes too. The disappearance of one of the  $\text{CF}_2$  twisting mode (327  $\text{cm}^{-1}$ ) for perfluorohexane at 8.2 GPa suggests the freezing of twisting motion due to reduced volume at high pressure phase. The disappearance of (347  $\text{cm}^{-1}$ )  $\text{CF}_2$  Rocking mode for perfluoroheptane beyond 7.0 GPa supports the same. Like medium chain alkanes, the behavior of bending modes (385, 617  $\text{cm}^{-1}$ ) with pressure is same [33,34]. It is interesting that the appearance of  $\text{CF}_3$  Rocking mode (552  $\text{cm}^{-1}$ ) for perfluorohexane and all-trans bending modes (550, 617  $\text{cm}^{-1}$ ) for perfluoroheptane shows that the condensed phase of mid-chain perfluoroalkanes prefers to have all-trans conformation. All these bending modes are belongs to more globular zigzag conformers. Behavior of these modes indicates that the high pressure phase beyond 8.2 GPa comprises only all-trans conformation [39]. The disappearance of the 552  $\text{cm}^{-1}$  mode near 8.2 GPa for perfluorohexane and 550  $\text{cm}^{-1}$  mode beyond 7.0 GPa for perfluoroheptane indicates that the  $\text{CF}_3$  vibrations are getting arrested due to volume reduction with high pressure (see Fig. 6). One could observe that the bending modes persist till 12 GPa indicates reduced degree of freedom along the molecular axis due to volume reduction at high pressure phase. The four Raman modes belong to  $\text{CF}_3$  and  $\text{CF}_2$  stretching vibrations are responsible for conformational change and closed packing of the molecules in different physical states. For perfluorohexane, the bands (996, 1220  $\text{cm}^{-1}$ ) which are disappearing at 8.2 GPa belong to less stable isomers. It is evident that the persistence of (719, 768  $\text{cm}^{-1}$ ) all-trans conformers beyond 8.2 GPa indicates that the high pressure phase only contains well-ordered all-trans conformers (see Fig. 7). The behavior of these modes of perfluoroheptane is also same. This has been proved by earlier reports [10,11,35]. In addition the qualitative intensity ratio [35]  $I_{763}(\text{TTT})/I_{993}(\text{TTC})$  for perfluorohexane

and the intensity ratio  $I_{756}(\text{TTTT})/I_{916}(\text{TTGT})$  for perfluoroheptane indicates the positive slope which is due to the presence of all trans conformers in the high pressure phase (see Fig. 9). In the case of C–C stretching region, the disappearance of 1380  $\text{cm}^{-1}$  and 678  $\text{cm}^{-1}$  beyond 8.2 GPa indicates that the high pressure phase of perfluorohexane dense packed with only distorted all-trans conformers. The disappearance of both of these end gauche modes (647, 1372  $\text{cm}^{-1}$ ) beyond 7.0 GPa for perfluoroheptane indicates more stable all-trans conformers only present in the system (see Fig. 8). This suggests that the structural transition beyond 8.2, 7.0 GPa for both the compounds could be due to disorder–order transition. This has been reported in temperature dependent vibrational spectroscopy studies on medium chain perfluorocarbons [10,11,41]. So it has been revealed that, there is an increase in all-trans conformers with reduced gauche defect with high pressure. Upon further increase in pressure, most of gauche modes disappear. This indicates that the highly stable population is all-trans in the high pressure phase of perfluorocarbons.

## Conclusions

In conclusion, high pressure Raman spectroscopic studies on perfluorohexane and perfluoroheptane performed up to 12 GPa. We were able to observe two phase transitions for perfluorohexane. They are as follows: (1) liquid–solid transition at 1.6 GPa, (2) solid I transition at 8.2 GPa. And also three phase transitions were observed for perfluoroheptane. They are as follows: (1) liquid–solid transition at 1.3 GPa, (2) intermediate solid I transition at 3.0 GPa, (3) solid II transition at 7.0 GPa. It has been proved from the Raman mode behavior with pressure, that the solid phase of these perfluoroalkanes comprises more than one conformer beyond crystallization. But the percentage of all-trans conformers is more. The change in slope ( $d\omega/dP$ ) of Raman bands shows that the solid I transition at 3.0 GPa could be the conversion of mid-gauche defect into trans conformers for perfluoroheptane. This structural transition could not show any drastic change in the Raman spectra. This shows that there is no change in the molecular structure. The disappearance of the modes suggests that the presence of less conformer in the system at high pressure. The intensity ratio  $I_{763}(\text{TTT})/I_{993}(\text{TTC})$  for perfluorohexane and the intensity ratio  $I_{756}(\text{TTTT})/I_{916}(\text{TTGT})$  for perfluoroheptane also give the qualitative information about the conformer population at the respective physical states with high pressure. The disappearance of most of the gauche conformer modes beyond 8.2, 7.0 GPa indicates their instability at high pressure phase of mid-chain perfluoroalkanes. It is evident that the high pressure phase of both the compounds beyond 8.2, 7.0 GPa tends to have close packing with distorted all-trans conformers. The phase transition beyond 8.2, 7.0 GPa could be disorder–order transition. High pressure X-ray diffraction is a prominent tool to explain more about this kind of structural transition.

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