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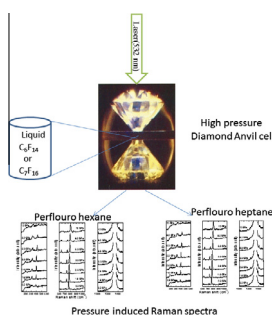
Comparative high pressure Raman studies on perfluorohexane and perfluoroheptane [☆]

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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 ω , $d\omega/dP$ 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 μm diameters. Perfluorocarbons were loaded in the gasketed diamond anvil cell along with <20 μm ruby chip as a pressure sensor. The pressure was calibrated by ruby R_1 line fluorescence method [19] with the accuracy of about ± 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) ≈ 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 μm 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 N₂ 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 cm^{-1}) of perfluorohexane and perfluoroheptane at ambient conditions and at high pressures. The Rayleigh frequency cut off for edge filter is around 100 cm^{-1} and further use of dichroic mirror for back scattering geometry made us unable to get the low frequency modes below 100 cm^{-1} . The presence of first order diamond peak at 1300 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) CF₂ Wagging, Twisting and Rocking region (275–350 cm^{-1}), (3) CF₂ and CF₃ Bending and Rocking region (350–620 cm^{-1}), (4) CF₂ and CF₃ Stretching region (700–1300 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 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 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 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

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