**Crystallization and phase transitions of** **C6H6 : C6F6 complex under extreme conditions using laser-driven shock**

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**Abstract:**

The C6H6 : C6F6 cocrystal is one of the simplest organic cocrystals with a molecule having a C-F bond and without any hydrogen bonding. It has a crystal structure very different from its constituents, C6H6 and C6F6, and its higher melting point indicates its increased stability relative to these two materials. So far, no studies are available on the phase transitions of this interesting adduct under dynamic compression. In this study, we present the findings of phase transitions of an equimolar mixture of C6H6 : C6F6 observed under rapid shock compression at pressures of up to 4.15 GPa using time-resolved Raman spectroscopy (TRRS). The compression is driven by a 2 J Nd: YAG laser with an 8 ns pulse length. Four prominent modes at 370 cm-1 (ν10F mode), 443 cm-1 (ν6F mode), 560 cm-1 (ν1F mode) and 991 cm-1 (ν1H mode) exhibit blue shift with scaling factors of 2.41 cm-1/GPa, 2.26 cm-1/GPa, 2.39 cm-1/GPa and 2.67 cm-1/GPa respectively. The Liquid → Solid-I phase transition is observed at around 0.49 GPa shock pressure. The second phase transition from Solid-I → Solid-VI is observed between 1.32 GPa and 2.60 GPa and no signature of the Solid-V phase is observed unlike in the case of static compression (see reference 1). Another phase transition Solid-VI → Solid-VII is observed between 3.9 GPa and 4.15 GPa. The shock velocities in the sample at two laser intensities, 1.47 GW/cm2 (300 mJ) and 2.46 GW/cm2 (500 mJ) are calculated by measuring the intensity ratio of Raman modes emerging from the shocked region to that of the whole sample and are 3.13 km/s and 4.05 km/s respectively. To compare with the experimental results, 1-D radiation hydrodynamics simulations are also performed. The experimental and simulated shock velocities are in good agreement. The mode Grüneisen parameter for the ν1H, ν1F, ν6F, ν10F and ν’10F modes are *γi* = 0.011(2), 0.022(2), 0.011(1), 0.024(3) and 0.379(14) respectively.

**Keywords:** Time-resolved Raman Spectroscopy, Phase-transition, Laser-driven shock, Benzene : Hexafluorobenzene co-crystal.

1. **Introduction:**

Interactions between aromatic compounds are of great importance in organic as well as biological studies. Despite having very similar structures, benzene (C6H6) and hexafluorobenzene (C6F6) interact very differently [1]. Benzene has an electron-rich carbon ring; while due to the high electronegativity of fluorine, the carbon ring in hexafluorobenzene is electron deficient [2]. The solid adduct formed upon mixing the two has a melting point of 25 °C, while that of benzene and hexafluorobenzene is 5.5 °C and 5.2 °C [3] respectively. This indicates that the adduct has a higher stability than its constituents and that its molecular arrangement is also significantly different. Amongst all organic co-crystals, C6H6 : C6F6 is one of the simplest co-crystals containing a molecule with C-F bond and without hydrogen bonding. Our understanding of the cohesion and intermolecular interactions in these materials has changed considerably over time. Earlier, such solids used to be thought of as ‘charge-transfer solids’ based on the donor-acceptor mechanism or π-π interaction between benzene and hexafluorobenzene [3, 4]. But, internal vibrations of the molecules in such adducts only show a small frequency shift in comparison to those of pure solids [5, 6]; hence, such mechanisms are not really supported by spectroscopy. A more acceptable mechanism of cohesion is based on the favorable interaction of quadrupole moments [7]. C6H6 has a large negative quadrupole moment while C6F6 has a largely positive one. Hence, they form a stable cocrystal due to favorable quadrupole interactions.

Formation of C6H6 : C6F6 cocrystals have been a subject of research since the 1960s [8] till date. In the recent past, various experimental and theoretical work such as neutron scattering [9, 10], Raman [11, 12] and IR spectroscopy [13], X-ray diffraction [11, 1], and density functional theory (DFT) – molecular dynamics (MD) [14] on C6H6 : C6F6 mixtures under extreme pressure and at different temperatures have been performed. J. H. Williams et al. [12] demonstrated three low-temperature phases at ambient pressure namely phase-II (*l2/m*), -III (*P*), and -IV (*P21/a*) at 260 K, 215 K, and 30 K respectively. Under static high pressure up to 20 GPa in a Diamond Anvil Cell (DAC) and at ambient temperature, Phase-V (*P21/c*), -VI, -VII, and -VIII were identified and above 20 GPa, pressure-induced polymerization of the adduct was observed [1]. The crystal structures of high-pressure phases (V-VIII) are different from those of low-temperature phases (II-IV). But, the phase transitions of this interesting co-crystal have neither been investigated under co-occurring extreme conditions of temperature and pressure nor under shock compression. In this work, we investigate the phase transitions of the C6H6 : C6F6 equimolar mixture using laser shock compression for the very first time.

Laser-based shock compression has two inherently distinct characteristics in comparison to traditional diamond anvil cell (DAC) based compression: One, laser shock compression ubiquitously involves high temperatures (along the Hugoniot) which allows us to explore off the isotherm phase transitions in the material; and two, the compression is extremely rapid (at the laser pulse width time scale) which can yield different phase transition mechanisms/routes in quite a few materials including hexafluorobenzene [14-17]. It has been found that the phase transition mechanism in quite a few materials depends on the time-scale of compression. C. Yuan et al. [15] studies the dependence of phase transitions on time-scale of compression of CCl4. Suzuki et al. [16] demonstrated that on slow compression of C6F6 at room temperature, a dendrite phenomenon was observed (beyond 0.3 GPa) and it further solidifies to phase-I (at 1 GPa) and into phase-II (at about 2-4 GPa); on the other hand, it solidifies directly into phase-II on the quick application of pressure up to 0.8 GPa. Also, laser-based shock compression allows for time-resolved studies (Time-Resolved Raman Spectroscopy and Time-Resolved X-ray Diffraction) enabling researchers to investigate and understand the dynamic phenomena which occur on nanosecond, or sub-nanosecond time scales (which encompass a great many chemical reactions and related phenomena).

Benzene [18] and hexafluorobenzene [17] have, earlier, been investigated under laser shock compression. This study presents the findings of laser-shock compression and time-resolved Raman spectroscopy of an equimolar mixture of benzene and hexafluorobenzene. 1D radiation hydrodynamics simulations have also been performed to understand the experimental data better and to verify experimentally determined shock velocity.

1. **Experimental details:**

The experiments were conducted at the TRRS (Time-Resolved Raman Spectroscopy) facility at HP&SRPD, B.A.R.C. Mumbai. This facility makes use of a high-power Q-switched Nd: YAG laser (2 J / 8 ns) in a pump-probe configuration. The pump beam (1064 nm, 8 ns), which carries most of the laser energy and has a tailored top spatial hat profile for spatially uniform shock generation, is focused on the glass-aluminum interface (focal spot diameter =1.8 mm) driving a shock wave into the aluminum foil. The pump energy is varied from 40 mJ (0.20 GW/cm2) to 1100 mJ (5.41 GW/cm2) in steps throughout the experiment resulting in a peak pressure range of 0.22 GPa to 4.15 GPa. The second harmonic probe beam (532 nm, 1.8 mJ / 5 ns), on the other hand, is focused to a diameter of 500 μm on the center of the focal spot of the pump beam to probe the shocked material that is least affected by transverse gradients in the hydrodynamic variables.

During the experiment, the sample is maintained in a confined geometry which has been proven [19] to enhance the shock amplitude by up to six times and enable the shock to be sustained for up to ten times longer. It consists of a cover glass (20 mm diameter, 2.5 mm thick) which has a 25 μm thick aluminum foil glued onto it followed by a 200 μm spacer which defines the sample thickness. It is followed by a glass rear window (identical to the cover glass) which completes the aforementioned confined geometry. A schematic of the target geometry is shown in figure 1. As mentioned earlier, the pump beam is focused onto the cover-glass: aluminum interface resulting in the ablation of the aluminum surface. As the ablated plasma is restricted from expanding in the backward direction by the cover glass, it imparts an enhanced shock wave into the aluminum foil. Due to the optimized thickness of the aluminum foil relative to the laser pulse length, the shock wave reaches peak amplitude in the aluminum foil and then crosses over into the sample. Due to the lower shock impedance of the sample in comparison to the aluminum, the amplitude of the shock wave reduces upon its entry into the sample. Due to the propagation of this shock wave, the sample gets dynamically compressed. Concurrently, the probe beam is focused on the sample from the other end. The delay between the pump and probe beams can be controlled by adjusting the number of round trips taken by the probe beam between two plane-parallel mirrors placed 1.05 meters apart (equating to a roundtrip time of 7 ns).

The scattered probe beam is captured by the collection optics and fed into a half-meter-long spectrometer followed by a gated ICCD (intensified charged coupled device) camera with 2048 x 512 pixels. A step filter is used to cut off the scattered Rayleigh signal. For higher spectral resolution, a 1200 gr/mm grating is used which provides a resolution of 3 cm-1 and for the higher temporal resolution, the ICCD gating time is kept to 2.5 ns. To capture the Raman signal with an excellent signal to noise (S/N) ratio, a total of 50 shots are taken for each spectrum resulting in a total accumulation time of 125 ns. The target assembly is set up on an X-Y-Z motorized stage to expose a fresh part of the sample for each new shot. A detailed schematic and description of the experimental set-up can be found in earlier works [20].

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**Fig. 1.** Schematic of the confinement geometry used in our experiment.

Benzene (purity > 99%) and Hexafluorobenzene (purity 99.9%) were procured from Sigma-Aldrich and used for experiments without any further purification. The C6H6 : C6F6 equimolar mixture is prepared at standard temperature and pressure (STP) and is in the liquid phase. As the temperature is lowered i.e., < 25 °C, it forms dendrite structures/co-crystals (phase-I, 𝑅3̅𝑚). The phase-I crystal structure is made up of columns of alternating benzene and hexafluorobenzene molecules arranged perpendicular to the threefold axis in a rhombohedral lattice as predicted by J. H. Williams [12] and shown in figure 2a. The blue lines in the figure link molecular centroids with their thickness being proportional to the magnitude of the total nearest neighbor pairwise interaction energy [12].

The equimolar mixture of the C6H6 : C6F6  sample forms initially as dendritic crystals at 22 °C (295 K), as shown in figure 2b, but as the crystallization continues it develops a much coarser polycrystalline texture (figure 2c) after 12 hours in the same laboratory conditions. During the experiments, the spectral range of 260 cm-1 – 1160 cm-1 is covered which enables us to record all of the important modes.



**Fig. 2.** **(a)** structure of solid-I phase of benzene: hexafluorobenzene cocrystal. The blue lines in the figure link molecular centroids with their thickness being proportional to the magnitude of the total nearest neighbor pairwise interaction energy [21] **(b)** dendrite formation and **(c)** crystallization of C6H6 : C6F6 equimolar mixture.

1. **Simulations:**

Simulations are performed using the one-dimensional Lagrangian radiation hydrodynamics simulation code HYADES [22]. HYADES employs a multi-group diffusion approximation for radiation transport and a flux-limited diffusion model for electron transport. For the glass and aluminum components of the target, SESAME [23] equation of state tables (SESAME: The Los Almos National Laboratory Equation-of-State database) is employed, for the C6H6 : C6F6 region a quotidian equation of state (QEOS) model [24] is employed. Opacities are calculated in-line using an average-atom model.

1. **Results and analysis:**

In our experiment, the sample is under rapid shock loading which imparts sudden extreme pressure and temperature to the sample. In subsequent sections, we present our observations under dynamic compression and its comparison with the results of static compression experiments performed by Y Wang, et al. [1]. Information regarding Raman modes assignment (at STP) in the studied spectral range is given in table 1 [1].

**Table 1.** Assignment of Raman modes of C6H6- C6F6 complex at STP.

|  |  |  |
| --- | --- | --- |
| Wavenumber (cm-1) | Intensity | Assignment |
| 370 | s | **ν10F** (C-F out-of-plane bending) |
| 443 | s | **ν6F** (C-C-C in-plane bending) |
| 560 | s | **ν1F** (Ring breathing) |
| 606 | w | **ν6H** (C-C-C in-plane bending) |
| 990 | vvs | **ν1H** (Ring breathing) |
| s: strong, w: weak, vvs: very very strong | | |

Two sets of experiments are performed. For the first set of experiments, the pump laser beam energy is set to 300 mJ (shock pressure ~ 1.32 GPa) and 500 mJ (shock pressure ~ 2.60 GPa), and the delay between the pump and the probe beams is varied from 10 ns to 94 ns to understand the buildup of shock pressure in the sample and to calculate the shock velocity at these laser energies. The obtained shocked Raman spectrum has contributions from both shocked and unshocked regions of the sample. To separate the contributions from these two regions, a multiple Lorentzian peak-fitting method is used in which the parameters (FWHM {Full Width at Half Maximum} and peak position) of the first peak are fixed to that of the unshocked Raman peak and the others are left free for best fitting. Then the obtained results are analyzed to investigate the distance that the shock wave has travelled for a particular time delay and hence the shock velocity in the sample. The shock velocity from the experiment is compared with the simulation results. The close agreement between the experimental results and the simulation values ensures that the other parameters such as the shock pressure and density of the shocked sample can be taken from the simulations. In the second set of experiments, the pump beam energy is varied from 40 mJ (shock pressure ~ 0.22 GPa) to 1100 mJ (shock pressure ~ 4.15 GPa) in steps while keeping the delay fixed (52ns for pump energies up to 700 mJ and 45 ns for higher pump energies). The delay is reduced at higher laser energies to avoid any interference of the reflected shock wave (coming from the sample : glass rear window interface) because, at higher laser energy, the shock pressure, and hence shock velocity, is higher in the sample. The delay is set in this way to get a significant signal from the shocked region of the sample and to avoid any interference from the reflected shock wave.

**IVa. Time delay analysis & calculation of shock wave velocity:**

To understand the propagation of shock wave through the sample and to verify the simulation results, time-delay experiments are performed at two laser energies: 300 mJ and 500 mJ by fixing the pump and probe energy and varying the delay between the two from 10 ns to 94 ns in steps of 7 ns or 14 ns. At both the laser energies, two intense modes at 560 cm-1 (ν1F)and 990 cm-1 (ν1H) have been analyzed in detail. Figures 3 and 4 show the analysis and simulation results at 300 mJ and 500 mJ laser energies respectively. Peaks in the experimental results have been color-matched with unshocked and shocked regions in the simulation results to enable easier interpretation.

At 300 mJ laser energy, at 10 ns delay between the pump and the probe beams, the experimental spectrum only shows an unshocked peak (figure 3a and 3b) and the simulation results (figure 3c) at 10 ns also confirm that the shock wave has not yet entered the sample. As the delay increased to 24 ns, the shock wave makes its entry into the sample and hence we see a new shocked (green) peak appearing at a higher wavenumber in both modes. On increasing the delay even further, the shock wave traverses deeper into the sample (the green region in figure 3c), and hence, the area under the shocked peak (green curve) goes on increasing. But, as the shock wave traverses farther, its amplitude decays slowly due to the onset of a rarefaction once the laser pulse is over. Due to this effect, the shocked peaks at higher delays exhibit a slight redshift. At 38 ns delay, both the signals from the shocked and unshocked sample are almost equal. This indicates that the shock wave has traversed almost half of the distance in the sample and the same can be seen from the simulation shown in figure 3c at 38 ns delay. At 73 ns delay, for *ν*1F mode shown in figure 3a, the Raman peak corresponding to the unshocked sample disappears and a new small peak (orange peak) appears at an even higher frequency. This indicates that the shock wave must have traversed the complete depth of the sample by around 70-71 ns and the reflected shock wave with higher amplitude (due to impedance mismatch) must have traversed some distance back into the sample causing a new peak to emerge at an even higher frequency. From the ν1H mode analysis at the same laser energy, as shown in figure 3b, it is observed that at 73 ns delay, the signal from the unshocked sample is negligible and the maximum contribution comes from the shocked region. This also indicates that the shock wave has traversed the sample completely by around 73-74 ns. The simulation results, shown in figure 3c, also show similar behavior. In the simulation, at 72 ns delay time, the reflected shock wave has traversed some distance back into the sample at higher pressure. The region covered by the reflected shock wave is represented in orange in the simulation results in figures 3 and 4 (c). This indicates that the simulated shock wave must have reached the sample–glass interface at some time around 69-70 ns. The experimental and the simulated shock transit times (i.e., shock velocities) are in close agreement. At further delays of 80 and 94 ns, both the Raman peaks due to the singly shocked region and the region traversed by the reflected shock wave are significantly redshifted due to the fast deterioration of the reflected shock wave as it propagates through the rarefaction wave caused by the passage of the forward going shock wave.

**Fig. 3. (a)** Lorentzian fit of shocked *ν*1F (560 cm-1) mode for different delay times at 300 mJ **(b)** Lorentzian fit of shocked *ν*1H (990 cm-1) mode for different delay times at 300 mJ **(c)** The spatial profile of shock waves at different delay times for laser energy of 300 mJ (obtained from 1-D radiation-hydrodynamics simulations). Red, green and orange colors correspond to unshocked, shocked and re-shocked regions respectively (both in peak fitting as well as simulation results).

Results for 500 mJ laser energy can also be explained in the same manner. At 500 mJ, the shock wave velocity is higher, and hence the exit times are shorter. At this energy, the exit time from the experimental results is about 56 - 57 ns (figure 4a and 4b) which is in close agreement with the simulated transit time of 58 ns (figure 4c).

**** **Fig. 4. (a)** Lorentzian fit of shocked *ν*1F (560 cm-1) mode for different delay times at 500 mJ **(b)** Lorentzian fit of shocked *ν*1H (990 cm-1) mode for different delay times at 500 mJ **(c)** The spatial profile of shock waves at different delay times for laser energy of 500 mJ (obtained from 1-D radiation-hydrodynamics simulations). Red, green and orange colors correspond to unshocked, shocked and re-shocked regions respectively (both in peak fitting as well as simulation results).

We also calculate the shock velocity from the simulation and experimental results as discussed here. From experimental results, the shock velocity is calculated by using the equation *Us = r.x* [25] where ‘*x’* is the sample thickness (200 µm) and ‘*r’* is the slope of the intensity ratio, vs. time delay curve (see figure 5a) where and is obtained by curve fitting of the experimentally obtained Raman spectra as shown in Figures 3 and 4. From simulations, the shock velocity is calculated by taking the slope of the Vcovered / Vtotal vs. time delay curve (see figure 5a) considering the fact that the Raman mode intensity is proportional to the volume of sample and multiplying it with sample thickness.

At 300 mJ, the experimentally obtained shock velocity is 3.3(1) km/s (ν1F mode) and 3.0(2) km/s (ν1H mode) which is fairly close to the shock velocity obtained from the simulation i.e. 3.3 km/s. While at 500 mJ, shock velocity from the simulation is ~ 4.2 km/s which can not be distinguished from the experimental results of 4.1(5) km/s (ν1F mode) and 4.02(2) km/s (ν1H mode). Hence it can be concluded that, overall, our simulations are in good agreement with the experimental results. It is anyway to be expected that the shock wave will propagate slightly faster in the 1-D simulations due to the absence of 2-D edge-loss mechanisms. Figure 5b shows the variation of the shock velocity (Us) with pressure. The dotted line is a linear fit to the simulation results. Us is obtained from the simulations, from time-delay analysis, and from the observed experimental exit times. All the values are in fairly good agreement with one another.

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**Fig. 5. (a)** The slope of the graph from the experimental and simulation data represents the shock wave velocities at laser energies of 300 mJ and 500 mJ respectively **(b)** Variation of Us with pressure (the dotted line is a linear fit to the simulation results).

**IVb. Raman analysis with varying shock pressure:**

Four Raman active modes [ν10F (370 cm-1), ν6F (443 cm-1), ν1F (560 cm-1), and ν1H (990 cm-1)] that fall in the spectral range 280 – 1100 cm-1 (shown in figure 6a) are studied extensively under varying dynamic compression by varying the pump beam energy from 40 mJ (~ 0.22 GPa) to 1100 mJ (~ 4.15 GPa) while fixing the time delay between the pump and the probe beams to either 52 ns (for lower energies) or 45 ns (for higher energies). The broad peak around 500 cm-1 is due to the quartz window. The results are analyzed using the multiple Lorentzian peak fitting methods described earlier. The Lorentzian peak fitting analysis of the shocked ν10F (375 cm-1) mode is shown in figure 6b. The peak fitting for other modes is done in similar fashion (we omit the details for the sake of brevity).

The C6H6 : C6F6 equimolar mixture is liquid at STP (Standard Temperature & Pressure) but when it is subjected to shock pressures of about 0.22 GPa, the intensities of the modes in the shocked condition are significantly larger than the signal from the unshocked condition; however, no narrowing of full width at half maxima (FWHM) of Raman modes is observed. This may be a possible signature of the beginning of a liquid to a solid phase transition. At 0.49 GPa pressure, the width of the shocked mode decreases compared to the unshocked mode, and also its intensity increases in comparison to the unshocked signal. Variation of FWHM and intensity of the ν10F mode with shock pressure are shown in Figures 7a and b respectively. This implies that the C6H6 : C6F6 equimolar mixture undergoes complete Liquid → Solid - I phase transition i.e., formation of C6H6 : C6F6 cocrystals occurs at this shock pressure. However, under static compression, this crystallization is observed at about 0.1 GPa [1]. The occurrence of this phase transition at a slightly higher pressure (in comparison to static DAC compression) is to be expected under shock compression because of the higher temperatures (shock compression follows the principle Hugoniot).

Under static compression [1], another phase transition Solid-I → Solid-V has been reported to occur at about 0.8 GPa. At this pressure, a new peak emerges at around 705 cm-1, originating from the out-of-phase motion of the benzene ring. However, from figure 6a, it can be seen that no such peak is to be observed at around 705 cm-1 in the case of shock compression. This indicates that the aforementioned phase transition doesn’t occur under shock compression.

On increasing the shock pressure to 1.32 GPa (300 mJ laser energy), broadening of the shocked peak at 370 cm-1 (ν10F) can be observed which indicates the emergence of a second peak at 388 cm-1 marked by the blue arrow in figure 6a and peak fitting graph shown in figure 6b. On increasing the pressure further to 2.60 GPa, this peak becomes a clear shoulder peak (marked by the green arrow). This is an indication of the onset of the Solid-I → Solid-VI phase transition. However, in the case of static compression, this phase transition reportedly occurs at 1.7 GPa which occurs from the Solid -V → Solid-VI phase. Both solid -V and Solid - VI phases also consist of alternately stacked C6H6 and C6F6 molecules, however, the stack is severely tilted [1]. Hence, it can be concluded that under rapid shock compression C6H6 : C6F6 cocrystals do not undergo Solid-I → Solid-V phase transition. On the further increase of the shock pressure to about 3.9 GPa, a shoulder peak emerges at 1008 cm-1 shown by the orange arrow in figure 6a, however, this shoulder peak merges with the ν1H peak and at 4.15 GPa, and a new peak at 465 cm-1 emerges (indicated by the cyan arrow). This indicates that C6H6 : C6F6 cocrystals undergo another phase transition viz. Solid-VI → Solid-VII occurring between 3.9 GPa and 4.15 GPa. Wang et al., have also reported a similar phase transition at 3.7 GPa in static compression measurements. In their case, they observed the emergence of three new peaks at 465, 714, and 1008 cm-1 in the spectral range of our study. In summary, Wang et al., reported four phase transitions up to 3.7 GPa pressure under static compression, and in our shock study, we observed three phase transitions in the dynamic pressure range 0.22 to 4.15 GPa. In the case of laser-driven shock compression, the phase transition Solid-I → Solid-V does not occur. Figure 8 shows the phase transitions under dynamic compression (from this study) along with low temperature phases [12] and room temperature high pressure phases [1]

From our experiment, we also observed that all the modes exhibit blue-shift under dynamic compression with the following scaling factors: ν10F = 370 + 2.41P(GPa) cm-1; ν6F = 443 + 2.26 P(GPa) cm-1; ν1F = 560 + 2.39 P(GPa) cm-1, and ν1H = 990 + 2.67P(GPa) cm-1. The scaling of the Raman frequency shift with the pressure of all the above-mentioned modes due to shock compression is shown in figure 6c along with the static compression results reported in ref [1]. Dotted vertical lines mark the observed phase transitions in our experiment. One interesting observation to note here is that the blue shift of the ν’10F peak (on Solid-I → Solid-VI phase transition) is much larger in shock compression than it is in static DAC compression. This mode may be sensitive to temperature.

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**Fig. 6. (a)** Raman spectra ofC6H6 : C6F6 equimolar mixture in the range 260 – 1100 cm-1 at various pressures. Arrows in the graph show the phase transitions **(b)** Lorentzian fit of shocked ν10F mode at different shock pressure. **(c)** Comparison of Raman shift obtained under shock and static compression (solid symbols represent shock compression data from our experiment and hollow symbols represent static compression data from reference [1]) in ν10F, ν6F, ν1F, and ν1H modes.



**Fig. 7.** Variation of **(a)** FWHM and **(b)** Intensity of ν10F mode with shock pressure.

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**Fig. 8.** Phase transitions in mixture observed at low temperature [12], at room temperature and high pressure [1] and at high temperature and high-pressure dynamic compression (this study).

**IVb. Mode Grüneisen parameters:**

The mode Grüneisen parameter is a non-dimensional quantity that is used to model the pressure dependency of vibrational frequencies (and hence properties) of a material. It has been shown to be inter-related with bond anharmonicity [26]. For the *i*th mode of a crystal, the mode Grüneisen parameter *γi* is mathematically represented as

…(1)

This formula, in itself, is considered to be a definition of the mode Grüneisen parameter because it directly provides a dimensionless representation of how a material responds to compression.

On integrating this equation and taking the natural log of both sides, we arrive at

…(2)

Where *V* is the volume of the bulk solid, is the vibrational wave number of the *i*th mode and 0 and P represent atmospheric pressure and applied pressure respectively. From equation 2, the slope of the log-log plot of relative frequency shift *vs.* relative volume change (or relative density change) for the *i*th vibrational mode gives us the Grüneisen parameter for that mode.

To calculate mode Grüneisen parameters, was obtained from curve fitting (figure 6) while was obtained from the simulations. The plot of relative frequency change *vs.* relative density change under shock compression for all the modes is shown in figure 9. Calculated mode Grüneisen parameter for the ν1H, ν1F, ν6F, ν10F and ν’10F modes are *γi* = 0.011(2), 0.022(2), 0.011(1), 0.024(3) and 0.379(14) respectively. Since the data is a continuous linear fit, the mode Grüneisen parameters are volume independent.

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**Fig. 9.** Log-log plot of relative frequency change *vs.* relative density change under shock compression for all the modes (ν10F, ν’10F,ν6F, ν1F, and ν1H).

1. **Conclusion:**

In this study, we have presented the findings of Raman studies on a benzene-hexafluorobenzene equimolar mixture when subjected to laser-driven shock compression up to 4.15 GPa. In total, four Raman active modes were investigated: 370 cm-1 (ν10F mode), 443 cm-1 (ν6F mode), 560 cm-1 (ν1F mode) and 990 cm-1 (ν1H mode) in the dynamic pressure range of 0.22 GPa to 4.15 GPa. Of the four modes, the ring breathing mode ν1H is the most intense and shows a blue shift of about 2.67 cm-1 / GPa, and the other modes also exhibit a similar blue shift. In total, three phase transitions were observed in the complex. A signature of Liquid → Solid-I phase transition (co-crystal formation) was observed at about 0.49 GPa through narrowing of the Raman peak and a concomitant increase in the Raman intensity. The second phase transition of Solid-I → Solid-VI was observed between 1.32 GPa and 2.60 GPa and the third phase transition (Solid-VI → Solid-VII) was observed between 3.90 GPa and 4.15 GPa. Phase transitions and Raman shift were also compared with the data from static compression of the mixture [1]. However, unlike the case of static compression, we could not observe the Solid-I → Solid-V phase transition. Hence, we can conclude that under rapid shock compression, the benzene-hexafluorobenzene co-crystal doesn’t undergo the Solid-I → Solid-V phase transition, instead, it goes directly from the Solid-I to the Solid- VI phase followed by a Solid-VI → Solid-VII phase transition at higher pressures. It would be interesting study to perform static high temperature studies on this mixture to de-convolute the effects of rapid compression from temperature.

Shock velocities were deduced by performing Time-Resolved Raman studies on ν1F and ν1H modes at 300 mJ and 500 mJ laser energies. At 300 mJ, the shock velocity comes out to be 3.3(1) km/s (ν1F mode) and 3.0(2) km/s (ν1H mode) and at 500 mJ, the shock velocity comes out to be 4.1(5) km/s (ν1F mode) and 4.02(1) km/s (ν1H mode). These velocities are in fairly good agreement with shock velocities obtained from 1-D radiation-hydrodynamics simulations which are 3.3 km/s (300 mJ) and 4.2 km/s (500mJ). The Grüneisen parameters corresponding to the ν1H, ν1F, ν6F, ν10F and ν’10F modes are *γi* = 0.011(2), 0.022(2), 0.011(1), 0.024(3) and 0.379(14) respectively.

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