Phase transitions in $C_{60} \cdot C_8H_8$ under hydrostatic pressure

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1 Introduction The highest symmetry member of the molecular cocrystal family $C_{60} \cdot C_8H_8$ was first synthesized by Pekker et al. [1]. The high stability of the 1:1 stoichiometry of $C_{60} \cdot C_8H_8$ is attributed to the perfect matching of the molecular geometry of the convex surface of fullerene and concave surface of cubane. Cubane molecules occupy the octahedral voids of the fcc C_{60} to form a stable $C_{60} \cdot C_8H_8$. Although $C_{60} \cdot C_8H_8$ is a relatively newly discovered material, the orientational ordering transition has been studied by different techniques. On cooling, $C_{60} \cdot C_8H_8$ undergoes an orientational ordering transition at 140 K [1]. At the transition, the symmetry lowers from fcc to orthorhombic. Pristine C_{60} is known to undergo a first-order orientational ordering transition associated with a change in crystal structure from fcc to sc at much higher temperature, namely at $T_c = 249$ K [2]. The lower transition temperature in $C_{60} \cdot C_8H_8$ compared to C_{60} is due to the ball bearing arrangement which facilitates easier rotation of the C_{60} molecule. By simulated annealing analysis of powder X-ray diffraction data the space group of the ordered orthorhombic phase was recently identified as *Pnma* [3]. Compared to C_{60}, this means that the nearest-neighbor fullerene–cubane interaction plays also an important role for the orientational ordering, in contrast to the earlier belief of the C_{60}–C_{60} interaction as the only driving mechanism of the transition [4].

Two pressure-induced anomalies in $C_{60} \cdot C_8H_8$ have been reported earlier based on high-pressure infrared measurements [5, 6]: The pressure-induced shifts of the vibrational modes show anomalies at 0.5 and 1.3 GPa. The first anomaly at 0.5 GPa was interpreted in terms of an orientational ordering transition of the fullerene molecules, while the second anomaly was attributed to the fullerene–cubane interaction. It has to be noted that these high-pressure infrared studies were carried out with a quasi-hydrostatic pressure transmitting medium (KCl). The solid pressure transmitting medium can cause strain effects on the samples, which can result in considerable mode broadening at high pressure. The mode broadening hindered the observation of splittings in Refs. [5, 6]. Therefore, better hydrostatic conditions are necessary to obtain a more detailed picture of the pressure effects in $C_{60} \cdot C_8H_8$.

This work is aimed to better understand the underlying mechanism that drives the orientational ordering transition
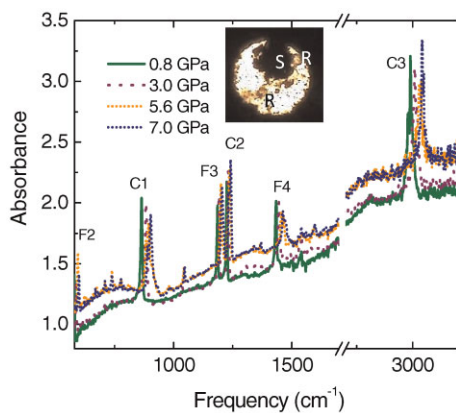
Figure 1 (online color at: www.pss-b.com) Midinfrared vibrational spectra of $C_{60} \cdot C_8H_8$ for selected pressures. Inset: Typical filling of the DAC with sample (S), ruby balls (R), and helium (bright region).

Figure 2 (online color at: www.pss-b.com) Fullerene (F) and cubane (C) vibrational modes of $C_{60} \cdot C_8H_8$ for selected pressures.

in $C_{60} \cdot C_8H_8$. Furthermore, infrared spectroscopy is very sensitive to symmetry changes in molecules. Thus, from the splitting of the vibrational modes, we can also deduce the site symmetry of the molecule which can indirectly verify the space group of the ordered phase. Helium was selected as the pressure transmitting medium, in order to follow the vibrational modes and their splitting up to high pressure. Moreover, the use of helium would bring out a more realistic critical pressure.

2 Experiment The synthesis of the $C_{60} \cdot C_8H_8$ co-crystals was described in detail by Pekker et al. [1]. High-pressure infrared measurements were performed up to 9.5 GPa with helium as hydrostatic pressure transmitting medium. A Syassen-Holzapfel type diamond anvil cell (DAC) was used to generate high pressures and a typical filling of the DAC with helium, the ruby ball, and the sample is shown in the inset of Fig. 1. Midinfrared (550–$8000\,\mathrm{cm}^{-1}$) transmission measurements (resolution $2\,\mathrm{cm}^{-1}$) were carried out with a Bruker IFS 66 V/s FTIR spectrometer combined with an infrared microscope. All measurements were performed at room temperature.

3 Results and discussion The $C_{60} \cdot C_8H_8$ has seven vibrational modes in the infrared region, of which six modes are clearly detected in the presented mid-infrared data. The fullerene (F) and cubane (C) vibrational modes of $C_{60} \cdot C_8H_8$ for selected pressures are depicted in Fig. 2. It can be clearly seen that even up to the highest measured pressure the vibrational modes remain very sharp and also mode splittings are observable. In comparison, with KCl as pressure transmitting medium the vibrational modes undergo significant broadening with increasing pressure [5, 6] and therefore the splittings are not resolvable. The vibrational modes are fitted with Lorentz oscillators to extract the frequencies with increasing pressure. The C3 mode has very high oscillator strength, which saturates at high pressure and prevents the analysis. Fig. 3 shows
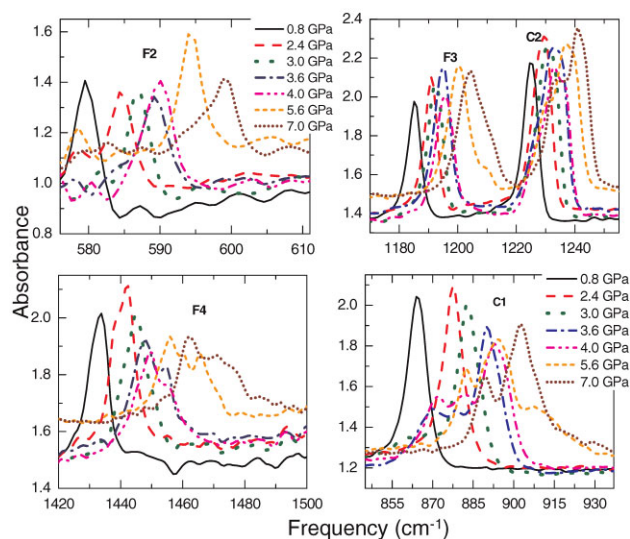
the pressure dependence of the fullerene and the cubane vibrational modes. In general, all vibrational modes harden with increasing pressure. Among the fullerene modes, the F4 mode shows a two-fold splitting at around 1 GPa. At 3 GPa, the F3 and F4 modes exhibit a three-fold splitting. Also the two observed cubane modes show a three-fold splitting at 3 GPa. It is interesting to note that the vibrational mode F2 remains a singlet up to high pressure.

The splitting of the cubane and fullerene modes at $P_c = 3$ GPa is interpreted in terms of the orientational ordering transition of the fullerene molecules. This transition is accompanied by a crystal symmetry change from fcc to orthorhombic. The orthorhombic phase with *Pnma* space group corresponds to a molecular site symmetry of D_{2h}, which is consistent with the observed threefold splitting of the T_{1u} modes. The driving force for the orientational ordering transition in $C_{60} \cdot C_8H_8$ can be attributed to both nearest-neighbor fullerene-cubane and C_{60}–C_{60} interactions in agreement with the recent results of Bortel et al. [3]. The value of P_c (3 GPa) derived from our data is considerably higher than the one reported (0.5 GPa) in the earlier work [5, 6]. Thirunavukkuarasu et al. attributed the transition at 0.5 GPa to orientational ordering and the anomaly at 1.3 GPa to fullerene-cubane interaction. However, a possible mode splitting was obscured by the broadening of the vibrational modes. According to our results, we rather attribute the previously reported anomaly at 1.3 GPa to the orientational ordering transition.

The good hydrostaticity of helium ensures a reliable determination of the transition pressure as it does not produce local strain effects on the sample in contrast to solid pressure transmitting media. However, additionally one has to take into account that helium can diffuse into the voids of the $C_{60} \cdot C_8H_8$ lattice, which could affect the transition pressure. The question related to diffusion of helium into the
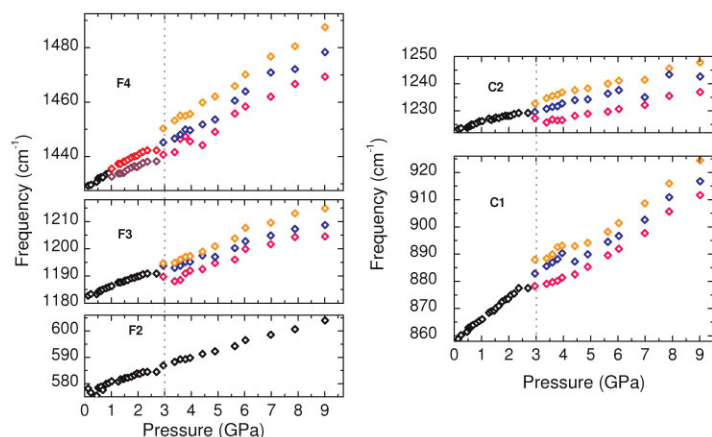
Figure 3 (online color at: www.pss-b.com) Pressure-dependent frequencies of the fullerene (F) and the cubane (C) vibrational modes of $C_{60} \cdot C_8H_8$. The dotted line marks the orientational ordering transition pressure ~ 3 GPa.

voids of fullerene-based compounds is briefly reviewed in the following. The influence of various hydrostatic pressure media, such as helium, nitrogen or argon, on the pressure-induced phenomena was extensively studied in the parent compound C_{60} [7, 8]. In fcc C_{60}, for each fullerene molecule in the lattice there are two tetrahedral and one octahedral voids with average diameters of 2.2 Å and 4.2 Å, respectively [9]. Any impurities in the voids can considerably affect the properties such as the orientational ordering transition temperature or pressure, compressibility, thermal expansion coefficient, etc. [8]. Sundqvist *et al.* summarizes the results of the orientational ordering transition boundary from various experiments; with the solid pressure transmitting medium it occurs at 0.5 GPa compared to a slightly higher value of 0.8 GPa for helium as pressure medium [10]. Furthermore, experiments have clearly suggested that helium with an atomic radius of 0.93 Å [11, 12] can penetrate both the octahedral and tetrahedral voids of the fcc C_{60} lattice and influences the orientational motion of the molecules. First, helium penetrates the octahedral voids rapidly and then the tetrahedral voids [8]. In case of C_{60} helium diffusion into the lattice increases the orientational ordering transition temperature by 10 K and the change in lattice parameter at the transition is halved [8]. Moreover, the intercalation is much more rapid with increasing pressure [8]. Therefore, the pressure transmitting medium and its hydrostaticity can play a key role in high pressure experiments on C_{60} based compounds.

In $C_{60} \cdot C_8H_8$ the octahedral voids of the fcc C_{60} are occupied by C_8H_8 and the tetrahedral voids are vacant for hosting the helium. Nevertheless, the influence of the intercalated helium on the transition pressure is expected to be weak and would only shift the pressure to a slightly higher value, similar to the case of C_{60}. In case of pristine C_{60} the critical pressure changes only by 0.3 GPa due to helium in the octahedral and tetrahedral voids, in contrast to a solid medium. Moreover, helium can only intercalate into the tetrahedral voids in case of $C_{60} \cdot C_8H_8$, so the influence of the intercalated helium on the critical pressure would be small. Thus, in the presented data on $C_{60} \cdot C_8H_8$ with helium as pressure medium the orientational ordering transition

pressure observed is reasonable. Also in carbon nanotubes an ideal critical pressure was reported with helium as pressure medium which is about 1 GPa higher than critical pressure with solid medium [13]. With the above argument it is justified that the observed threefold splitting at 3 GPa is the orientational ordering transition which is driven by the intermolecular interactions.

Further evidence for the orientational ordering transition at 3 GPa is the activation of silent modes due to the symmetry reduction from fcc to orthorhombic. Figure 4(a) shows the activated silent modes close to the C1 mode at 3 and 8 GPa. The silent modes harden with increasing pressure [see Fig. 4(b)]. Other silent modes activated under pressure are also observed in the region 700–800 cm^{-1} (see Fig. 5). This serves as additional evidence that the symmetry lowers at
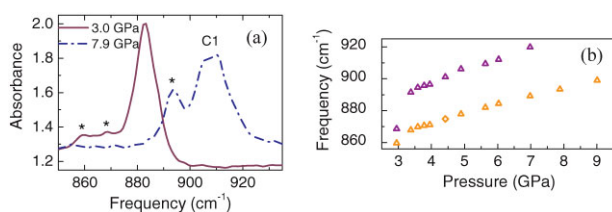

Figure 4 (online color at: www.pss-b.com) (a) Silent modes (marked with ∗) close to the C1 vibrational modes for selected pressures and (b) pressure dependence of the frequencies of these silent modes.
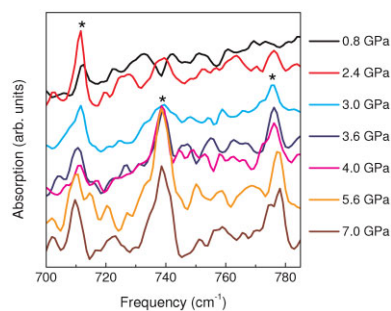

Figure 5 (online color at: www.pss-b.com) Activation of silent modes (marked with ∗).

3 GPa in connection with the disorder-order transition in $C_{60} \cdot C_8H_8$.

The $C_{60} \cdot C_8H_8$ pressure-temperature phase diagram reported by Iwasiewicz-Wabnig et al. has an orientational ordering transition line marked based on the pressure coefficient of pure C_{60} [14]. According to this P-T diagram, the ordering transition at room temperature would occur at around 1 GPa. However, according to the present understanding the ordering mechanism in $C_{60} \cdot C_8H_8$ is not only driven by the nearest-neighbor C_{60}–C_{60} interaction, but also the nearest-neighbor fullerene-cubane interaction plays an important role. By taking this and additional experimental results into account, the orientational ordering transition in the P-T phase diagram of $C_{60} \cdot C_8H_8$ should occur at a higher P_c at 300 K than indicated in the P-T diagram of Ref. [14]. This is also consistent with the lower transition pressure found in C_{60} nanotubes [15].

At 1 GPa, only the F4 mode splits, and this can be explained in terms of the appearance of the silent modes under pressure. Kamarás et al. [16] have discussed the appearance of forbidden vibrational modes in the solid state C_{60}. The presence of the crystal field in the fcc crystal reduces the point group I_h of the C_{60} molecule to T_h site symmetry. This causes the activation of some silent odd-parity modes. At ambient conditions, these effects are weak due to the dynamical orientational disorder whereas with lowering the temperature several modes appear in the infrared spectrum. Similarly with increasing pressure, the vibrational modes can appear such as the one observed very close to the F4 mode at 1 GPa, which is weak and is seen more as a shoulder of the F4 mode. This mode can be interpreted in terms of the G_u mode and should not be confused with a splitting of the F4 mode itself. The G_u mode is very weak and could not be followed well when the F4 mode undergoes a three-fold splitting at 3 GPa. Similarly, at $710\,cm^{-1}$ a weak H_u mode appears at around 0.8 GPa (see Fig. 5). Finally, the robustness of the F2 mode has already been discussed in literature based on temperature-dependent measurements [16]. Thus it is not surprising that no splitting of the F2 mode was observed under pressure.

4 Conclusions In summary, the vibrational properties of $C_{60} \cdot C_8H_8$ were investigated under high pressure with helium as pressure transmitting medium. At 3 GPa the three-fold splitting of the fullerene and cubane vibrational modes signal the orientational ordering transition, which is driven by both the nearest neighbor fullerene-cubane and C_{60}–C_{60} interactions. The threefold splitting of fullerene and cubane modes can be attributed to the D_{2h} molecular site symmetry, which is consistent with the *Pnma* space group of orthorhombic crystal symmetry in the ordered $C_{60} \cdot C_8H_8$ phase. Furthermore, the activation of silent modes is observed at 3 GPa confirming the critical pressure of the orientational ordering transition. Additionally, at around 1 GPa some weak modes are observed in the infrared spectrum due to the crystal field effect.

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