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Infrared spectroscopy on the rotor–stator compounds C_{60} – C_8H_8 and C_{70} – C_8H_8 under pressure

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1 Introduction

The fullerene–cubane molecular crystals C_{60} – C_8H_8 and C_{70} – C_8H_8 , which were synthesized only recently, are the first members of the rotor–stator crystal family [1]. At room temperature, C_{60} – C_8H_8 has a face-centered cubic (fcc) structure while C_{70} – C_8H_8 forms a body-centered tetragonal (bct) crystal. Static cubane molecules occupy the octahedral voids (elongated octahedron in case of C_{70} – C_8H_8) and act as bearings for the rotating fullerene molecules. Although there exists only a weak van der Waals interaction between the fullerenes and cubane, they form high-symmetry molecular crystals due to molecular recognition between the convex surface of fullerene and concave surface of cubane. These novel rotor–stator compounds therefore offer a great opportunity to understand the intermolecular interactions in fullerene derivatives.

At low temperature C_{60} – C_8H_8 and C_{70} – C_8H_8 undergo orientational ordering transitions at 140 K and 150 K, respectively, where the rotational degrees of freedom of the fullerene molecules become restricted [1, 2]. The orientational ordering temperature in C_{60} – C_8H_8 is much lower than for other fullerene derivatives, which can be attributed to the increased interfullerene distance in C_{60} – C_8H_8 [2]. Consequently, in fullerene–cubane molecular crystals pressure-induced phenomena are expected to occur at higher pressure compared to other fullerene derivatives and pristine C_{60} .

Recently, the pressure-induced phase transitions in C_{60} – C_8H_8 were investigated by pressure-dependent transmittance measurements in the infrared frequency range [3]. It was found that the orientational ordering of the C_{60} molecules in C_{60} – C_8H_8 indeed occurs at a pressure of about 0.8 GPa, which is

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significantly higher than for pristine fullerene. Here, we present more detailed spectroscopic data on the pressure-induced phenomena in $C_{60}-C_8H_8$ and also show corresponding results for the compound $C_{70}-C_8H_8$.

2 Experiment

The $C_{60}-C_8H_8$ and $C_{70}-C_8H_8$ powder samples were synthesized by evaporating aromatic solutions of fullerenes and cubane or by adding isopropyl alcohol as precipitant [1]. The pressure-dependent transmittance measurements were performed at room temperature using a Bruker IFS 66v/s spectrometer with an infrared microscope (Bruker IRscopeII). The pressure was generated by a diamond anvil cell (DAC) and the ruby luminescence method was used for pressure determination [4]. The pressure-dependent transmittance was studied for pressures up to 10 GPa in the far- and mid-infrared frequency range: The intensity $I_s(\omega)$ of the radiation transmitted by the mixture of powder sample and the pressure transmitting medium (KCl) was measured. As reference, the intensity $I_r(\omega)$ transmitted by the pure pressure transmitting medium inside the DAC was used. The transmittance was then calculated according to $T(\omega) = I_s(\omega)/I_r(\omega)$. The absorbance is calculated as $A = \log_{10}(1/T)$.

3 Results and discussion

Since only weak van der Waals interaction between the molecules is present, the characteristic vibrational modes of the fullerene molecules can be observed in the infrared spectra of $C_{60}-C_8H_8$ and $C_{70}-C_8H_8$ without any frequency shift compared to pure C_{60} and C_{70} , together with the three characteristic modes of cubane [5–8]. A few selected vibrational modes in the infrared absorbance spectra of $C_{60}-C_8H_8$ and $C_{70}-C_8H_8$ for different pressures are shown in Fig. 1. The interference fringes in the spectra are due to multiple reflections of the incident infrared radiation within the DAC. For both $C_{60}-C_8H_8$ and $C_{70}-C_8H_8$ the response of the vibrational modes of the fullerene molecules to increasing pressure is very similar to that of the pristine fullerenes. In addition to the pressure-induced frequency shifts, the vibrational modes are broadened and damped by the application of pressure. However, the vibrational modes of fullerenes and cubane can be clearly observed up to the highest applied pressure of

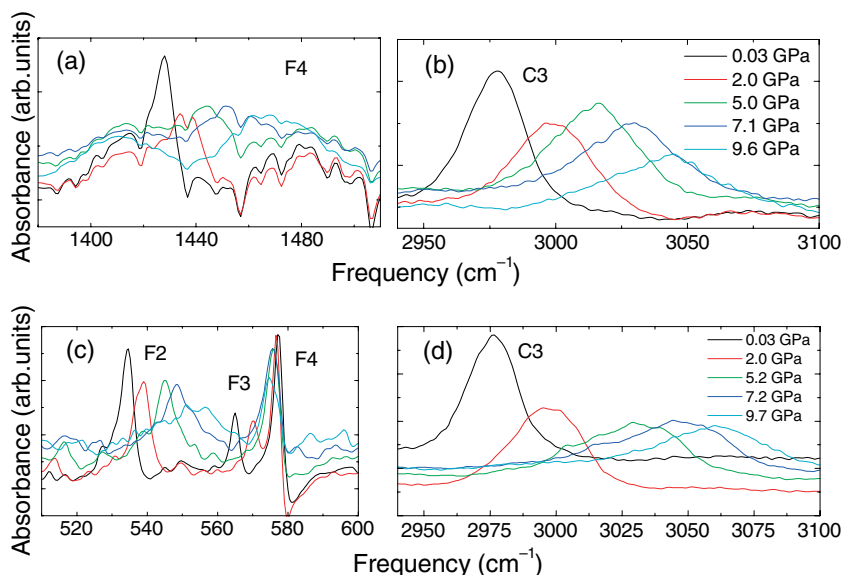


Fig. 1 (online colour at: www.pss-b.com) Infrared absorbance spectra of $C_{60}-C_8H_8$ [(a) and (b)] and $C_{70}-C_8H_8$ [(c) and (d)] as a function of pressure. Fullerene modes are denoted by F, cubane modes by C.

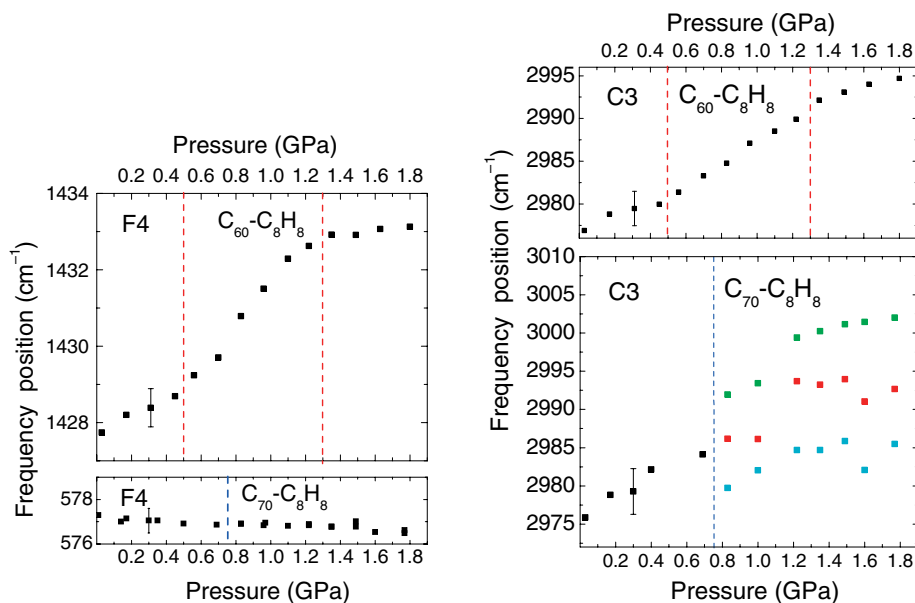


Fig. 2 (online colour at: www.pss-b.com) Pressure-dependent frequency positions of the vibrational modes F4 and C3 of $C_{60}-C_8H_8$ and $C_{70}-C_8H_8$ in the low-pressure regime (<2 GPa). The vertical dashed lines indicate the pressures of the phase transitions.

about 10 GPa. Furthermore, the pressure-induced changes in the vibrational modes are reversible upon pressure release.

In order to find possible signatures of the orientational ordering phase transitions in the absorbance spectra of $C_{60}-C_8H_8$ and $C_{70}-C_8H_8$, the positions of the vibrational modes were extracted by fitting with Lorentzian functions and plotted as a function of pressure. As examples, we present in Fig. 2 the frequency positions of the vibrational modes F4 (fullerene mode) and C3 (cubane mode) of $C_{60}-C_8H_8$ and $C_{70}-C_8H_8$ as a function of pressure up to 2 GPa. The vibrational modes exhibit linear frequency shifts with changes in the slope at certain pressures. For $C_{60}-C_8H_8$ two anomalies are found: the first anomaly occurs at 0.5 GPa, and the second one at around 1.3 GPa. The value of the first anomaly is somewhat lower than observed in our earlier study [3], but agrees perfectly with recent Raman data by Sundqvist et al. [9]. For $C_{70}-C_8H_8$ we observe a splitting of the C3 vibrational mode into three lines at around 0.8 GPa, whereas for the F4 mode no anomaly is obvious.

The pressure–temperature phase diagram of pristine C_{60} can give insight into the possible nature of the observed anomalies in $C_{60}-C_8H_8$. The orientational ordering transition in C_{60} , where the crystal structure changes from fcc to simple cubic (sc), is well studied. This transition occurs at 0.2 GPa at room temperature. Furthermore, a second anomaly was reported at around 2 GPa in several experimental studies [7, 10–12]. However, the values of the critical pressure of this second transition obtained by different experiments are not consistent, and the origin of this transition is still unclear. It is well known that an increase in pressure has a similar effect on the physical properties of materials as a decrease in temperature. The two anomalies in C_{60} at 0.2 GPa and 2 GPa, both reversible upon pressure release, were therefore attributed to an fcc-to-sc and a glassy transition, respectively, in accordance with the temperature-dependent orientational ordering transition at 260 K and the glass transition at 90 K, respectively [10, 11]. However, the pressure range of the second phase transition suggests that this transition is more likely related to a change in the orientational ordering of the fullerene molecules, namely from so-called **P** to **H** orientation [13]. Therefore, we tentatively attribute the anomaly at 0.5 GPa in $C_{60}-C_8H_8$ to the occurrence of an orientational ordering of the fullerene molecules, and the second anomaly at around 1.3 GPa to a pressure-induced change of the orientational order.

The pressure dependence of the vibrational modes in $C_{70}-C_8H_8$ is different from that in $C_{60}-C_8H_8$ in two respects (see Fig. 2): (i) the fullerene F4 mode is hardly affected by the pressure application, and (ii) the cubane C3 mode splits into three lines. Possible reasons for this behavior can be inferred from the temperature-dependent structural study on $C_{70}-C_8H_8$ [2]. At room temperature the free rotation of the C_{70} molecules is restricted and the basic motion is a uniaxial rotation around the long molecular axis (C_5). In addition, the long axis precesses around the c -axis of the tetragonal unit cell. Below 150 K the precession of the long axis is frozen, while the uniaxial rotation of the fullerene molecules persists; the cubane molecules are orientationally ordered. This temperature-dependent orientational ordering in $C_{70}-C_8H_8$ is accompanied by a structural phase transition.

In accordance with our findings for $C_{60}-C_8H_8$, we ascribe the anomaly at around 0.8 GPa in $C_{70}-C_8H_8$ to a pressure-induced orientational ordering transition. The fullerene modes show no anomalous behavior with respect to pressure (see pressure dependence of the F4 mode of $C_{70}-C_8H_8$ in Fig. 2 as an example), indicating that the fullerene molecules are hardly affected by the orientational ordering. This could be explained by the fact that the C_{70} molecules are still rotating around the frozen long axis in the orientationally ordered phase, i.e., they are less affected by the pressure-induced changes in the crystal structure. The static cubane molecules, in contrast, experience an increased anisotropy in the local environment with increasing pressure. Hence, the observed splitting of the cubane mode is probably due to pressure-induced changes in the crystal symmetry and enhanced intermolecular interactions.

4 Conclusion

The infrared absorbance spectra of the rotor–stator compounds $C_{60}-C_8H_8$ and $C_{70}-C_8H_8$ under pressure suggest the occurrence of orientational ordering phase transitions at 0.5 and 0.8 GPa, respectively. For $C_{60}-C_8H_8$ a second anomaly is found in the pressure dependence of the vibrational mode frequencies at around 1.3 GPa, which we attribute to pressure-induced changes in the orientational order of the C_{60} molecules. For $C_{70}-C_8H_8$ the orientational ordering transition is indicated by a splitting of the C3 cubane mode into three lines, in contrast to the fullerene modes which show no anomalies with increasing pressure. The observed mode splitting is probably due to an anisotropic local environment of the cubane molecules caused by pressure-induced changes in the crystal symmetry and enhanced intermolecular interactions.

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