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Pressure-dependent infrared spectroscopy on the fullerene rotor–stator compound C_{60} – C_8H_8

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1 Introduction

The recently synthesized fullerene–cubane C_{60} – C_8H_8 molecular crystals constitute rotor–stator systems, where the static cubane, C_8H_8 , occupies the octahedral interstices of the face-centered-cubic structure and acts as a bearing between the rotating fullerene C_{60} molecules [1]. C_{60} – C_8H_8 undergoes an orientational ordering phase transition at around 140 K, where the rotation of the fullerenes stops. This transition temperature is significantly lower than in any other fullerene derivative. It was suggested [2] that this might be due to the combination of the high symmetry environment of fullerenes, the perfect match of convex fullerene and concave cubane molecular surfaces, and the significantly expanded fullerene lattice. According to the latter aspect, i.e., the weaker interaction between the fullerene molecules, a pressure-induced orientational ordering transition is expected to occur at a higher pressure compared to, e.g., solid C_{60} . In order to test this hypothesis, we carried out pressure-dependent transmission measurements at room temperature to search for the signatures of a pressure-induced structural phase transition.

2 Experiment

Powder of C_{60} – C_8H_8 was prepared as described in Ref. [1]. For the pressure measurements, the C_{60} – C_8H_8 powder was mixed with the pressure transmitting media, namely polyethylene and KCl for the far-infrared and mid-infrared frequency range, respectively. A diamond anvil cell (DAC) was used for the generation of pressures up to 10 GPa. The pressure in the DAC was determined by the ruby lumines-

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cence method [3]. Pressure-dependent transmittance experiments were conducted at room temperature using a Bruker IFS 66v/S FT-IR spectrometer with an infrared microscope (Bruker IRscope II).

The pressure-dependent transmittance was studied in the far- and mid-infrared frequency range: the DAC was filled with the mixture of C_{60} - C_8H_8 powder and pressure transmitting medium, and the intensity $I_s(\omega)$ of the radiation transmitting the mixture 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 given by $A = \log_{10}(1/T)$.

3 Results and discussion

The infrared spectrum of C_{60} - C_8H_8 consists of seven vibrational modes, three of C_8H_8 [4] and four of C_{60} [5], all of T_{1u} symmetry, in accordance with the high-symmetry point groups of the two species (O_h for cubane and I_h for C_{60}). Changes in the infrared spectrum upon symmetry lowering have been studied extensively, for cubane derivatives with several sidegroups [4] and for fullerene solids below the orientational ordering temperature [6] and in various polymers [7]. For the latter, the region between 700 and 800 cm^{-1} proved to be a sensitive indicator of symmetry because of the many silent modes becoming activated. We have observed these signatures in the copolymer of cubane and C_{60} obtained by annealing C_{60} - C_8H_8 [1], and in C_{60} - C_8H_8 below the orientational phase transition [8]. Since it is known that increasing pressure in fullerenes has a similar effect on many physical properties as lowering the temperature, including the orientational phase transition [9], we expect to observe changes in the infrared spectra with pressure as well.

The infrared absorbance spectra of C_{60} - C_8H_8 at the lowest and highest pressure are shown in Fig. 1. The vibrational modes are superimposed on interference fringes due to multiple reflections of the incident radiation between the two diamond anvils of the DAC. It is apparent that pressure causes several striking changes in the spectrum. The new lines appearing in the 700–800 cm^{-1} range can be assigned to previously silent fullerene modes becoming IR-active due to symmetry lowering. The observation that the newly activated silent modes become comparable in intensity to the T_{1u} -derived modes further strengthens the analogy with other low-symmetry systems: photopolymers [10] and high-temperature-high-pressure polymers [7]. Such a symmetry lowering can have several origins, as already mentioned. In this case fullerene–fullerene polymerization is excluded for steric reasons. Furthermore, the cubane peaks are still preserved at 10 GPa, indicating that a reaction between cubane and C_{60} has not taken place. Thus the most plausible explanation for the spectral changes is an orientational phase transition where the rotation of the fullerene molecules stops. Since the cubane cubes are not rotating, this transition obviously will affect the cubane vibrations much less. In fact, Fig. 1 shows that the cubane peaks are much more pronounced at the highest pressure than the fullerene peaks.

All principal peaks show a pronounced hardening upon pressure application, except for F1. (The downshift of the F1 peak is known for pristine C_{60} from previous studies [11].) We obtained the pressure-

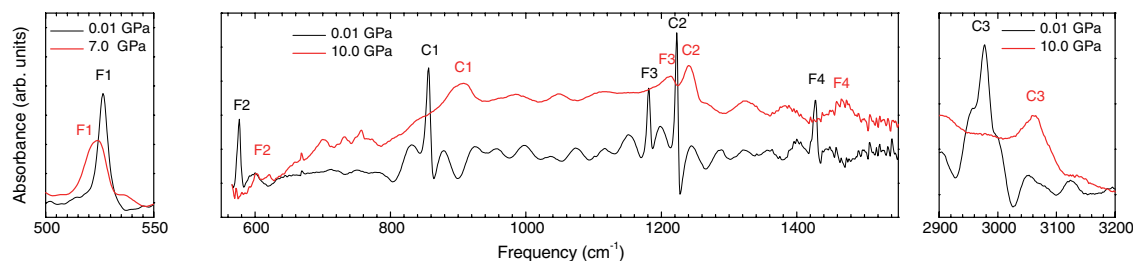


Fig. 1 (online colour at: www.pss-b.com) Infrared absorbance spectra of C_{60} - C_8H_8 as a function of pressure. Fullerene modes are denoted by F, cubane modes by C (black for low pressure, red for high pressure). Note that the absorbance scale is different in the different panels.

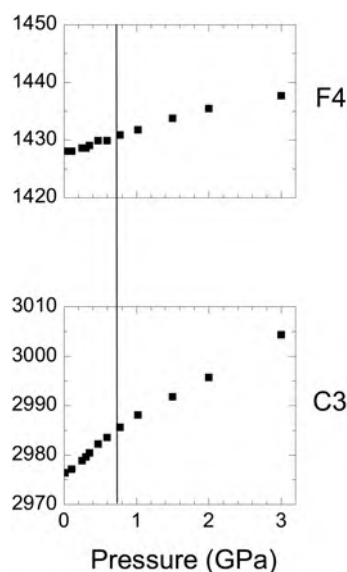


Fig. 2 Pressure dependence of the positions of one fullerene (F4) and one cubane (C3) T_{1u} mode in $C_{60}-C_8H_8$. The vertical line denotes the pressure where we estimate the orientational ordering transition to occur.

dependent frequency positions of the vibrational modes by fitting with Gaussian functions. In Fig. 2 we plot the resulting positions of one fullerene (F4) and one cubane (C3) vibrational mode as a function of pressure. Starting from the lowest pressure, the modes exhibit a linear frequency shift with increasing pressure. A detailed analysis, however, reveals a kink in the pressure dependence at a pressure of ≈ 0.8 GPa, and above this pressure the linear pressure coefficient is changed [8]. These findings support the assumption of a structural phase transition at around 0.8 GPa, affecting both types of constituents.

The obtained results should be compared with the pressure-temperature phase diagram of the pristine fullerene. C_{60} undergoes an orientational ordering transition from a face-centered cubic to a simple cubic phase at 260 K [12]. In comparison, in $C_{60}-C_8H_8$ this transition occurs at a considerably lower temperature (140 K). In general, the orientational temperature decreases with increasing free volume in fullerene solids. This is in agreement with the increased fullerene nearest-neighbor distances in $C_{60}-C_8H_8$ [1]. Following the same line of argument, a larger interfullerene distance should lead to an enhanced pressure at which the orientational ordering takes place. With a non-intercalating pressure-transmitting medium the orientational ordering transition in C_{60} occurs at around 0.2 GPa at 300 K [13, 14]. Our value of 0.8 GPa is indeed much higher. Both effects – the lower transition temperature as well as the higher transition pressure – could thus be explained in terms of the expanded lattice in the $C_{60}-C_8H_8$ compound, as earlier suggested [2].

It would be premature to speculate on the possible temperature-pressure phase diagram based on these two points, especially since the analogy with pristine fullerenes [9] is not applicable here, the dominant interaction being that between cubane and fullerene, not between fullerene molecules. However, the higher transition pressure has important practical implications: the rotator phase can be studied at room temperature in a wider pressure range than in any other fullerene solid. (As pointed out in Ref. [9], most pressure studies at room temperature only reflect the properties of the static phase because the transition pressure is close to the lower limit of common pressure cells.)

Another interesting aspect is the robustness of the vibrational modes in $C_{60}-C_8H_8$ against pressure. According to Fig. 1 most of the modes attributed to C_{60} (denoted by F) are suppressed at the highest applied pressure. In contrast, the cubane modes (denoted by C) survive, although broadened, up to the highest pressure. The enhanced robustness of the cubane modes against pressure might be due to the considerable shielding of the C_8H_8 molecules from pressure in the interball voids in the crystal.

4 Conclusions

In conclusion, from our infrared absorbance spectra of the novel rotor–stator compound C_{60} – C_8H_8 as a function of pressure we could extract the pressure dependence of the frequencies of the molecular vibrations. The kinks in the pressure dependence suggest the occurrence of an orientational ordering transition at around 0.8 GPa at room temperature. The qualitative features of the spectra at high pressure indicate a symmetry lowering of the fullerene molecules, as expected in a static phase where the molecular rotations stop. The higher transition pressure as well as the lower transition temperature in C_{60} – C_8H_8 compared to C_{60} could be attributed to the expanded lattice. The cubane vibrational modes survive up to a higher pressure compared to the C_{60} modes, suggesting a considerable shielding of the C_8H_8 molecules from pressure in the interball voids in the crystal.

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