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Low-temperature optical studies of C_{60} -cubane rotor-stator compound

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Abstract. We present here low-temperature Raman and photoluminescence spectra of the C_{60} cubane rotor-stator compound. We show the continuous evolution of Raman spectra between 77 K and room temperature, with no sharp transition visible at 140 K, the orientational ordering temperature. Low-temperature luminescence spectra of C_{60} in C_{60} -cubane compound are found to be shifted and better resolved then spectra for pristine C_{60} at the corresponding temperatures, showing relatively weaker intermolecular interactions. In fact, the solid-state luminescence of C_{60} -cubane is similar to free-molecule C_{60} luminescence spectra.

1. Introduction

Nearly-spherical C_{60} molecules form a face-centered cubic (f.c.c.) lattice with large voids. It was recently demonstrated that nearly cubic, slightly concave cubane (C_8H_8) molecules can be inserted into octahedral voids in the fullerene lattice creating a rotor-stator compound [1,2]. The C_{60} -cubane compound was structurally characterized [1,3] and found to polymerize at high temperature due to the poor thermodynamic stability and high reactivity of cubane [1,4]. High-pressure–high-temperature studies by *ex situ* Raman spectroscopy and X-ray diffraction have revealed a rich phase diagram/ reaction map [5,6], and an infrared spectroscopy study under pressure has also been reported [7]. C_{60} -cubane is reported to undergo a first order phase transition at 140 K [1,3], where C_{60} molecules become orientationally ordered, leading to a lowering of the lattice symmetry from f.c.c. to orthorhombic at low temperatures. In this report we show the evolution of the optical properties of C_{60} -cubane at low temperatures, covering both structural phases.

2. Experimental details

 C_{60} -cubane compound was prepared by crystallization from solution by the method described in Ref. [1]. Sublimed C_{60} , studied for comparison purposes, was stored and handled under Ar gas atmosphere, shielded from light in order to avoid photopolymerization. C_{60} and C_{60} -cubane were studied in separate experiments. Several small crystals were chosen for each experiment and loaded into an optical access cryostat (Linkam cell) under Ar gas. Care was taken to minimize the amount of water vapour present inside the Linkam cell to prevent ice freezing onto samples and the optical access window, but we

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were unfortunately not able to eliminate all the water and usually a very thin ice layer was visible. The samples were placed on an Ag surface whose temperature was controlled electronically by electric heating and liquid nitrogen cooling. The temperature was slowly ramped between the desired values and samples were allowed to reach thermal equilibrium with the Ag surface before measurements. The total temperature range covered was 77-300 K.

Raman and photoluminescence (PL) spectra were recorded with a Renishaw 1000 grating spectrometer equipped with three excitation lasers: a 514.5 nm Ar^+ laser, a 632.5 nm He-Ne laser and a 780 nm diode laser. We have tried to collect Raman spectra with all three lasers, obtaining good results with both Ar^+ ion and diode laser. As noted in earlier studies [5,6], He-Ne excitation gave a very strong luminescence background and thus a very poor Raman signal-to-noise ratio. Photo-luminescence spectra were excited by Ar^+ or He-Ne lasers and recorded in units of wavenumber down-shift with respect to the original laser line, later recalculated to absolute wavelengths.

3. Results

3.1. Low-temperature Raman spectra

Raman spectra of C_{60} -cubane show C_{60} peaks at positions nearly identical to those observed for pristine C_{60} , showing the very weak intermolecular interactions. In many cases cubane peaks are also visible at 905 and 1000 cm⁻¹ [8]. Figure 1 shows low temperature data recorded using the diode laser, which provided spectra with clearly visible cubane peaks, very well resolved low-frequency C_{60} Raman modes, and a very small luminescence background. Apart from the cubane modes, the only obvious difference between these spectra and those from pure C_{60} is that the $H_g(1)$ mode is always seen to be split when using the diode laser. As discussed earlier [6], we believe that this corresponds to vibrations with the symmetry axis pointing at or between neighbouring molecules, respectively.

Panels in fig. 1 show the evolution in the peak positions of the $H_g(1)$, $A_g(1)$, $H_g(4)$ and $A_g(2)$ modes of C_{60} and the E_g and $A_g(1)$ modes of cubane. Only very small shifts are observed in the peak positions of C_{60} modes with T or on crossing the 140 K phase transition line, while cubane mode positions seem completely independent of T. Since the C_{60} peaks shift continuously downward with increasing temperature, it is not possible to assign distinct, characteristic peak positions to each material phase.



Figure 1. Raman spectra of C_{60} · C_8H_8 at low temperatures, as indicated. Only the strongest modes are shown and each inset is labelled with the mode name. Spectra are vertically shifted for clarity.

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Raman spectroscopy, often used to identify the polymeric phases of pure C_{60} [9], cannot distinguish between the polymeric phases of C_{60} -cubane [5,6]. The present low-temperature results show that the same applies to the two equilibrium phases of the material. The Raman spectra for these two phases are very similar, and it is impossible to use these to identify the structural phase of the material.

3.2. Photoluminescence

Due to the possible differences in focus quality, the presence of a thin water layer and small variations in its thickness (visible but not possible to quantify) at different temperatures, the PL spectra presented here were arbitrarily scaled, setting the maximum intensity in each case to 1. The spectra thus provide a good qualitative source of information but quantitative comparisons may be inaccurate. PL spectra excited in C_{60} -cubane and in pristine C_{60} crystals by Ar^+ ion and He-Ne lasers were very similar in range (see figure 2), therefore we conclude that the PL of C_{60} -cubane between about 650 and 850 nm is due to the C_{60} molecules in the compound, with no cubane PL evident.

We found earlier [5,6] that the high energy Ar^+ ion laser did not photopolymerize C_{60} -cubane, but caused local destruction or evaporation of cubane. With this laser, cubane peaks could be observed only using very short exposure times at very low power [6]. We believe that the striking similarity between the PL of pure C_{60} and the Ar^+ ion laser excited PL of C_{60} -cubane in figure 2 is due to same effect, i.e. cubane loss due to the Ar^+ ion laser. The true PL spectrum for the C_{60} -cubane compound is thus believed to be that excited by the He-Ne laser, shown in the upper panels of figures 2 and 3.



Figure 2. Comparison of PL spectra of C_{60} · C_8H_8 and C_{60} excited by Ar^+ and He-Ne lasers at 77 K.

Figure 3. PL spectra of C_{60} -cubane (top) and pristine C_{60} at selected temperatures. The lattice structures are also indicated.

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Figure 3 shows PL spectra of C_{60} -cubane and C_{60} recorded at various temperatures. We show the 77 K and 273 K spectra, in order to contrast the low- and high-temperature behaviour of both materials. The C_{60} data agree well with data from literature [10]. We also show PL spectra for both materials just below and just above their respective low-temperature transitions, i.e. the orientational ordering transition at 140 K in C_{60} -cubane, and the 261 K rotational ordering transition and the 90 K rotational freezing ("glass transition") for pure C_{60} . For both materials rotational arrest leads to the appearance of sharp peaks in the spectra. C_{60} has a rich vibronic structure, leading to a large number of PL transitions over the band gap. Also, symmetry-breaking mechanisms override the selection rules and a meaningful spectral analysis is very difficult. However, although we have not yet been able to identify the observed peaks it is clear that the PL spectra might be more useful than the Raman spectra to identify the structural states and the phase transitions in C_{60} -cubane.

The PL spectrum of solid C_{60} -cubane obtained at 77 K has a much better resolution than the corresponding PL spectrum of crystalline C_{60} and shows features usually only seen in PL spectra from C_{60} molecules in solution or isolated in rare gas matrices [10,11]. This unusual behaviour must be a consequence of very weak intermolecular interactions relative to those in pure solid C_{60} . The effective crystal field felt by each C_{60} molecule in the compound material is clearly almost negligible, and the molecules behave as if they were free. The physical isolation of C_{60} molecules from their neighbours by interstitial cubane is similar to the effect of very low temperature; spectra of C_{60} -cubane at liquid nitrogen temperature are comparable to those of solid C_{60} obtained at much lower temperatures [12].

4. Conclusions

We find that the measured PL spectra of C_{60} -cubane are potentially much more useful than the corresponding Raman spectra for identification of the structural state and the phase transitions at low temperatures. Furthermore, at liquid nitrogen temperature the PL spectra of C_{60} -cubane are similar to those for free molecular C_{60} , showing a peak resolution accessible for solid C_{60} only at extremely low temperatures. We attribute this to the extremely weak intermolecular interactions. A full comparative study of C_{60} -cubane and pure C_{60} might lead to a better understanding of interactions in molecular solids, i.e. in which way a specific solid-state environment affects molecular properties.

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