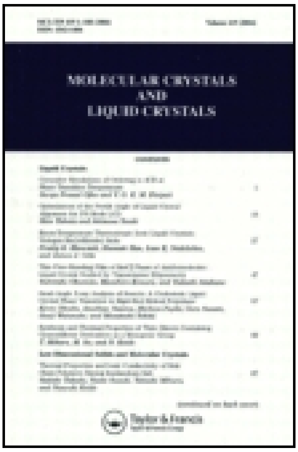

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A Study of Reversible Photochemical Phenomena in C_{60}

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A STUDY OF REVERSIBLE PHOTOCHEMICAL PHENOMENA IN C_{60}

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Abstract We report Raman measurements on the photoinduced disassociation via a metastable excited state intermediate of the photoproduct formed from the photochemical degradation of C_{60}. At low intensities, the intrinsic 1468cm^{-1} C_{60} mode softens to 1459cm^{-1}, which is stable below an apparent threshold intensity above which it shifts abruptly to 1463cm^{-1}. This mode is stable with increasing intensities. Upon a return to low intensities, the 1468cm^{-1} intrinsic C_{60} line reappears. The positioning of the Raman line at 1463cm^{-1} is associated with an excited state intermediate, observable only at high excitation densities.

INTRODUCTION

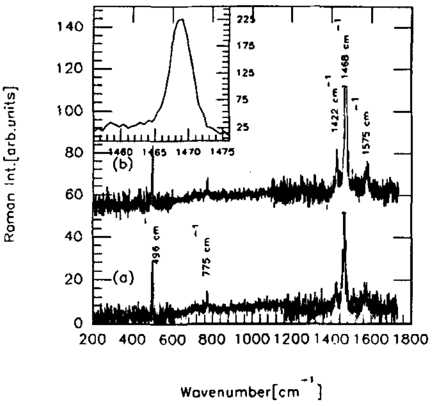
The Raman spectrum of C_{60} is dominated by ten Raman active molecular vibrations[1], whose frequency positioning has been a point of dispute. The dispute has focused on the strong A_g pentagonal pinch mode, observed at either 1468 or at 1459 wavenumbers[2,3]. A comparison of spectra recorded in air and those under argon indicated that a positioning of the mode at 1468cm^{-1} was oxygen induced. However, it appears that all of the C_{60} molecular modes are sensitive to laser irradiation[4,5] and are observed in inert atmosphere to irreversibly soften approximately 10cm^{-1}. Such prolonged illumination renders the C_{60} insoluble[5] and strong C_{120} and C_{180} peaks are seen in mass spectra. The process appears to be a photochemical degradation of the material. This has led to the proposal of a 2+2 cycloaddition across π-bonds of neighbouring molecules, a "photopolymerisation" process[5], which occurs through a molecular excited state. Oxygen acts as an excited state quencher which inhibits the photodegradation process[4,5]. Rao et al.[5], have observed a thermal depolymerisation of the photoproduct at temperatures of >100°C. We report the photo-driven depolymerisation of the C_{60} polymer via the formation of an intermediate excited state species associated with the 1463cm^{-1} Raman feature.

RESULTS AND DISCUSSION

Sample preparation and the experimental parameters have previously been discussed[4,6]. All samples were measured under argon unless otherwise specified and at room temperature with the 514.5nm Ar^+ laser line with crystals mounted on copper substrates to prevent heating and films deposited on quartz.

Fig. 1 shows a C_{60} oxygen-free (a) and oxygenated (b) film Raman spectra taken after ten seconds illumination at 1mW(50W/cm^2). The 1468cm^{-1} C_{60} A_g mode[1] is observed in both spectra to be the dominant Raman feature and is intrinsic to the material. Upon prolonged illumination of the oxygen-free film, the 1468cm^{-1} Raman line and in fact all of the modes are seen to undergo an irreversible shift of 10cm^{-1} downfield, which has been associated with the polymerisation of the C_{60}. The formation of the photoproduct is also seen with minimal illumination (100µW) indicative of a time-dependent process.

Fig. 2 shows the expanded region around 1468cm^{-1}. The measurements are taken with continuous illumination on a single point on the crystal with increasing laser intensities. At 1mW, the 1468cm^{-1} Raman line has already photodegraded after 360sec and the 1459cm^{-1} photopolymer line, exhibiting lower intensity, is the sole new feature. This feature is stable for the length of the measurement (~25 minutes) and up to a certain intensity(b).At an apparent sample dependent threshold value of 14mW, the Raman line shifts to higher wavenumbers. A noncontinuous shift of the Raman line to a frequency of 1463cm^{-1} is observed. The position of this peak is insensitive to prolonged illumination time (~15 minutes) and highest intensities (19mW). No further frequency shifts are measured and no 1459cm^{-1} line is seen, suggesting the evolution to a mode seen only at higher excitation densities.



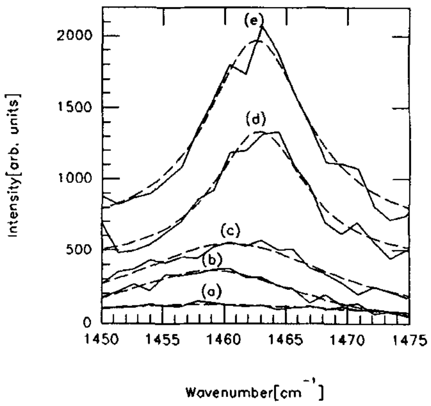


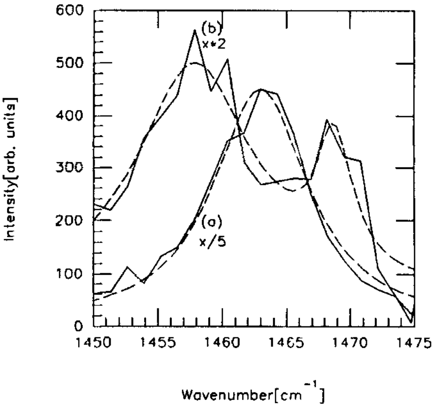
Fig.1: Raman spectra of (a)oxygen-free and (b)oxygenated films measured after 10sec at 1mW. Fig.2: Evolution of spectral features as a function of increasing intensity. (a)1mW; (b)9mW; (c)14 mW; (d)17mW; e)17.5mW. Dashed lines are the Lorentzian fits of the spectra(solid lines).

The shift from 1459cm^{-1} to 1463cm^{-1} is observed to be accompanied by a sharp rise in Raman peak intensity and the background luminescence, suggestive of a step-like process. The behaviours of both of these parameters are highly nonlinear and have been fitted with high order exponents (~10). The nonlinear intensity dependence of the evolution of the 1463cm^{-1} Raman line and the sudden rise in background luminescence distinctly separate it from that of the original C_{60} and the weakly luminescent photoproduct.

The 1463cm^{-1} Raman line is seen to return at low powers to the intrinsic C_{60} 1468cm^{-1} Raman frequency. The 1463cm^{-1} was produced at 15mW (fig.3(a)). The spot on the crystal was then blocked from further illumination and the laser power was then decreased to 5mW and measured on the same spot on the crystal. The 1468cm^{-1} Raman line is reproduced (fig.3(b)). The 1459cm^{-1} line is also seen and indicative of renewed degradation. In contrast, repeating the same experiment but at lower excitation densities, where the polymer alone is observed (fig.4(a)) and then measuring at 1mW reproduces the 1459cm^{-1} feature alone (fig.4(b)). Two separate behaviours are thus observed. The photoproduct associated with the 1459cm^{-1} line is irreversible at lower intensities and is thus of photochemical nature, seen at lower excitation densities. The 1463cm^{-1} species is the pathway through which the photoproduct breaks down into the monomer, or the C_{60} material and is thus of a photophysical, transient nature observed only at high excitation densities.

Raman intensities are dominated by π-electron polarisability and the force constant connected with the Raman frequency is associated largely with σ-bond character[7]. In the 1459cm^{-1} irreversibly phototransformed species, the mode softening from the 1468cm^{-1} A_g C_{60} feature is indicative of a loss of π-electron contribution to the force constant, and the reduced Raman intensity implies reduced radial polarisability of the π-system[7]. This is consistent with the formation of an intermolecular π-bond via a 2+2 cycloaddition[5]. The

1463cm^{-1} mode is softened with respect to the C_{60} mode at low intensities, indicative of a loss of π-electron contribution to the force constant, but the increased Raman intensity implies a greater π-electron polarisability, or delocalisation between the balls.



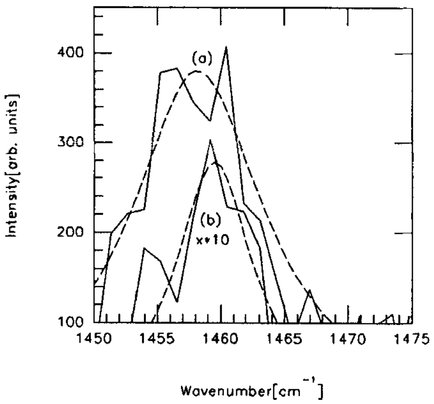


Fig.3: Spectra are taken at (a)15mW and (b)5mW. Fig.4: Spectra are taken at (a)9mW and (b)1mW. Dashed lines are the Lorentzian fits of the spectra(solid lines).

At low temperatures, where photopolymerisation is inhibited by the freezing out of the molecular rotations[5,8] van Loosdrecht et al. observed a reversible softening of the 1468cm^{-1} A_g pentagonal pinch mode with increasing laser intensities accompanied by a nonlinear rise in the luminescence[9]. The mode shifting and associated changes in both Raman intensity and background luminescence are noncontinuous and three distinct features(1468, 1463 and 1459cm^{-1}) are seen. The observation of the 1463 cm^{-1} feature at high excitation densities is consistent with the mode seen upon depolymerisation at high intensities. The nature of the intermediate state is unclear, but the nonlinear increase in the luminescence and increased π-electron delocalisation upon the evolution of the 1463cm^{-1} line positioning associate it with the reported nonlinear luminescence and photoconductive processes in C_{60}[6,10,11].

CONCLUSIONS

Optical studies on solid-state C_{60} reveal a photochemical degradation at low to moderate intensities. The process can be photo-reversed at high intensities. Photoinduced depolymerisation results in an intermediate metastable state, with a distinct Raman frequency, intensity and luminescence. This distinct photophysical behaviour prompts consideration of the photophysical processes in solid-state C_{60} at high excitation densities.

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