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## Raman and infrared studies of single-crystal C<sub>60</sub> and derivatives

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**Abstract.** We describe results of Raman and infrared studies of single crystals of pure C<sub>60</sub>, CS<sub>2</sub> solvated C<sub>60</sub> (C<sub>60</sub>·1.5CS<sub>2</sub>) and of (BEDT-TTF)<sub>2</sub>C<sub>60</sub> (BEDT-TTF is bisethylenedithio tetrathiafulvalene or ET). We have observed phonon shifts in the crystal surfaces using Raman scattering which we assign to diffusion of molecular oxygen into the crystals; our results indicate that the presence of molecular oxygen hinders rotation of C<sub>60</sub> molecules in the crystals. The four T<sub>1u</sub> vibrational modes in the infrared spectrum of pure C<sub>60</sub> show fine structure which we attribute to Fermi resonances. We show that C<sub>60</sub> vibrations in C<sub>60</sub>·1.5CS<sub>2</sub> crystals are less anharmonic than in pure C<sub>60</sub> crystals.

### 1. Introduction

A number of spectroscopic investigations have been reported on the fullerenes since their discovery by Kroto *et al* (1985) and the subsequent development of an efficient method for their production by Krätschmer *et al* (1990). The majority of this experimental work has been carried out on thin films or solutions of C<sub>60</sub>. We report here Raman and infrared spectra of single crystals of unsolvated C<sub>60</sub>, CS<sub>2</sub> solvated C<sub>60</sub> (C<sub>60</sub>·1.5CS<sub>2</sub>) and (BEDT-TTF)<sub>2</sub>C<sub>60</sub>, (BEDT-TTF or (ET) is bis(ethylenedithio)-tetrathiafulvalene; see Bryce (1991) for a review of the ET molecule and its charge transfer salts).

The structure of the C<sub>60</sub> molecule is well known, consisting of 60 carbon atoms arranged over the surface of a hollow cage in the form of a regular truncated icosahedron with symmetry group I<sub>h</sub> (Weeks *et al* 1989). The diameter of the molecule is 7.1 Å and the cage is built up of 12 pentagons and 20 hexagons, with each pentagon surrounded by five hexagons. The covalent bonds that are shared between a pentagon and a hexagon are longer than those shared by two hexagons (1.455 Å and 1.391 Å respectively). Each atom is bonded to its three nearest neighbours by one long and two short covalent bonds and the 60 carbon atoms are all equivalent.

NMR measurements at room temperature show that the C<sub>60</sub> molecules in unsolvated crystals are spinning with a rotational correlation time of ~9 ps (Tycko *et al* 1991). Neutron scattering investigations of solid C<sub>60</sub> revealed a phase transition at 250 K from a face-centred cubic (FCC) structure with a lattice parameter of 4.16 Å to a simple cubic (SC) structure (David *et al* 1992). The crystal undergoes a small lattice contraction at the transition and the molecules in the FCC unit cell become inequivalent, producing a SC unit cell containing four molecules. In the low temperature phase the C<sub>60</sub> molecules are orientationally ordered

so that the electron deficient regions (pentagon faces) of one molecule are opposite the electron rich bonds (hexagon-hexagon edges) of its neighbours. Between 250 K and 90 K the molecules undergo thermally excited rotational jumps between four (111) orientations at a much slower rate than the rotational motion above 250 K (David *et al* 1992). Below 90 K the molecules no longer rotate. Calorimetry measurements (Chung *et al* 1992) show that the transition at 250 K is first order. The Young's modulus has been shown to increase by 8% upon cooling through the 250 K transition (Shi *et al* 1992) corresponding to a discontinuous increase in the intermolecular interaction.

The crystal structure of C<sub>60</sub> depends upon the amount of C<sub>70</sub> and higher fullerenes present and also on the amount of solvent of crystallization present. A pristine unsolvated C<sub>60</sub> crystal, grown by sublimation, has a FCC structure at room temperature (Heiney *et al* 1991, Tycko *et al* 1991). Crystals of C<sub>60</sub> with ~10% C<sub>70</sub> grown from a benzene solution (solvated) were found to have a hexagonal close-packed (HCP) structure and to contain occluded benzene (Krätschmer *et al* 1990). Crystals grown from a pentane solution have a non-close-packed structure consisting of a twinned monoclinic cell with channels containing pentane molecules (Fleming *et al* 1991). Orthorhombic crystals of C<sub>60</sub> grown by Kikuchi *et al* (1991) from a CS<sub>2</sub> solution were found to contain occluded CS<sub>2</sub> and not to be as efficiently packed as the FCC or HCP structures. The composition of these crystals is C<sub>60</sub>·1.5CS<sub>2</sub> (Morosin *et al* 1991) with unit cell parameters

$$a = 24.97(6)$$

$$b = 25.52(3)$$

$$c = 9.98(1) \text{ \AA}$$

and there are eight C<sub>60</sub> molecules in the unit cell.

For pentane-solvated crystals, calorimetry and sound velocity measurements showed a second-order transition at 242 K with a width of 20 K (Chung *et al* 1992, Shi *et al* 1992). Sound velocity measurements on CS<sub>2</sub>-solvated crystals did not show a clear transition (Shi *et al* 1992). After annealing their CS<sub>2</sub>-solvated crystals above 200°C, Shi *et al* (1992) observed a sharp increase in the Young's modulus at 242 K. However the overall increase in the Young's modulus in all of these materials between room temperature and 100 K is very similar. NMR spectra from CS<sub>2</sub>-solvated crystals showed rotational narrowing below 77 K (Kikuchi *et al* 1991).

A recent x-ray study of (BEDT-TTF)<sub>2</sub>C<sub>60</sub> (ET<sub>2</sub>C<sub>60</sub>; Izuoka *et al* 1992) shows that the C<sub>60</sub> molecules lie between pairs of deformed ET molecules. Comparison of bond lengths at 150 K of the ET molecule with other known salts indicates that little charge is transferred. NMR measurements indicate that the C<sub>60</sub> molecules rotate isotropically in this material even at 190 K.

The vibrational modes of the isolated C<sub>60</sub> (I<sub>h</sub> point group) molecule have the following representations:

$$\Gamma = 2A_g + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + 1A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u$$

giving 46 distinct modes and a total of 174 vibrations when the degeneracies are taken into account. The two A<sub>g</sub> modes and the eight H<sub>g</sub> modes are Raman active and the four T<sub>1u</sub> modes are IR active. Some of the degeneracies of the vibrational modes of the isolated C<sub>60</sub> molecule are lifted in the crystalline environment and splitting of each of the modes of C<sub>60</sub>

Table 1.

| I <sub>h</sub>  | FCC phase                       | SC phase   |
|-----------------|---------------------------------|--|
| A <sub>g</sub>  | A <sub>g</sub>                  | A <sub>g</sub> + T <sub>g</sub>                    |
| T <sub>1g</sub> | T <sub>g</sub>                  | 3T <sub>g</sub> + A <sub>g</sub> + E <sub>g</sub>  |
| T <sub>2g</sub> | T <sub>g</sub>                  | 3T <sub>g</sub> + A <sub>g</sub> + E <sub>g</sub>  |
| G <sub>g</sub>  | A <sub>g</sub> + T <sub>g</sub> | 4T <sub>g</sub> + 2A <sub>g</sub> + E <sub>g</sub> |
| H <sub>g</sub>  | E <sub>g</sub> + T <sub>g</sub> | 5T <sub>g</sub> + 2E <sub>g</sub> + A <sub>g</sub> |
| A <sub>u</sub>  | A <sub>u</sub>                  | A <sub>u</sub> + T <sub>u</sub>                    |
| T <sub>1u</sub> | T <sub>u</sub>                  | 3T <sub>u</sub> + E <sub>u</sub> + A <sub>u</sub>  |
| T <sub>2u</sub> | T <sub>u</sub>                  | 3T <sub>u</sub> + E <sub>u</sub> + A <sub>u</sub>  |
| G <sub>u</sub>  | A <sub>u</sub> + T <sub>u</sub> | 4T <sub>u</sub> + 2A <sub>u</sub> + E <sub>u</sub> |
| H <sub>u</sub>  | E <sub>u</sub> + T <sub>u</sub> | 5T <sub>u</sub> + 2E <sub>u</sub> + A <sub>u</sub> |

in the FCC and SC crystal structures are expected as shown in table 1 (Dresselhaus *et al* 1992).

van Loosdrecht *et al* (1992) (see this reference for earlier work) have recently reported discontinuous changes in frequency and linewidth at the 250 K transition for several modes in the Raman spectrum of a freshly cleaved sublimed single crystal of C<sub>60</sub> and additional modes were observed on going from the FCC to the SC phase (see table 1). The highest energy A<sub>g</sub> and H<sub>g</sub> modes, which occur at 1459 and 1566 cm<sup>-1</sup> at room temperature, shift discontinuously at the 250 K transition to 1468 and 1575 cm<sup>-1</sup> and the lines become narrower. Narasimhan *et al* (1992) observed a gradual splitting of the highest energy T<sub>1u</sub> mode below the FCC-SC phase transition in the infrared absorption spectra of thin films of C<sub>60</sub>. Duclos *et al* (1991) observed shifts in frequency of the highest energy A<sub>g</sub> and H<sub>g</sub> modes in thin films at room temperature upon contamination with oxygen that were similar to the shifts observed by van Loosdrecht *et al* (1992) at the 250 K phase transition. In our studies we have focused primarily on the effects of oxygen on the dynamical properties of the C<sub>60</sub> molecules in single crystals of 'pure' C<sub>60</sub>, solvated C<sub>60</sub> (C<sub>60</sub>·1.5CS<sub>2</sub>) and ET<sub>2</sub>C<sub>60</sub>. In the following section we outline our experimental techniques and in section 3 we describe results of Raman and infrared measurements. In section 4 we discuss implications of our results.

## 2. Experimental details

The fullerenes used in this study were prepared at the Tokyo Metropolitan University by arc heating of graphite under a helium atmosphere of ~100 Torr. C<sub>60</sub>, C<sub>70</sub> and higher fullerenes were separated from the soot-like materials by HPLC (Kikuchi *et al* 1991). Single crystals of C<sub>60</sub> were then obtained at the Royal Institution by evaporation of a CS<sub>2</sub> solution at room temperature. The crystals obtained had typical dimensions 5 × 1 × 0.05 mm. These solvated crystals have occluded CS<sub>2</sub> and have orthorhombic symmetry (see section 1). The CS<sub>2</sub> solvent was removed and unsolvated single crystals of C<sub>60</sub> were produced by sublimation at 700 °C under a vacuum of 10<sup>-2</sup> Torr. Single crystals of typical dimension 0.5 × 0.3 × 0.3 mm condensed in the cold zone outside the furnace. Single crystals (black needles ~2 mm long) of ET<sub>2</sub>C<sub>60</sub> were obtained by slow evaporation of a carbon disulphide solution of C<sub>60</sub> and two equivalents of ET (i.e. one mole of C<sub>60</sub> to every two moles of ET).

All of these crystals had been exposed to the atmosphere for a period of weeks before the experiments on them described in this paper were performed. However, the  $\text{ET}_2\text{C}_{60}$  crystals were large enough to cleave so that Raman scattering measurements could be made from a fresh surface (the crystals were placed in helium atmosphere directly after being cleaved). The fresh crystal surface was then exposed to the atmosphere for a period of a week and the Raman scattering measurements repeated. It was found, as described below, that oxygen absorbed from the atmosphere had a significant effect upon the Raman spectrum of  $\text{C}_{60}$  in  $\text{ET}_2\text{C}_{60}$ . Crystals of unsolvated  $\text{C}_{60}$  were subsequently prepared and care was taken not to expose them to oxygen. These crystals were grown by sublimation under a dynamic vacuum of  $10^{-2}$  Torr, transferred to a capillary tube in an argon atmosphere and sealed with GE varnish.

Both polarized and unpolarized Raman spectra were measured in a quasi-back-scattering geometry, using a Spex 1877 triple-grating spectrometer with a liquid-nitrogen-cooled (CCD) camera detection system. All the visible lines of an  $\text{Ar}^+$ -ion laser and the 442 nm line from a He/Cd laser were used separately as the excitation source. The single-crystal samples were mounted inside a continuous flow cryostat in an atmosphere of helium. Raman spectra were taken between 4 K and room temperature. In order to minimize sample heating the intensity of the excitation laser was kept below 3 mW and not tightly focused. The Stokes–antiStokes intensity ratio of the lowest energy feature in the Raman spectrum was measured at room temperature with the green  $\text{Ar}^+$  laser lines, indicating sample heating of less than 10 K, independent of laser line.

IR absorption spectra were measured using a Perkin–Elmer 1710 infrared Fourier transform spectrometer together with a SpectraTech IR–PLAN infrared microscope. The measurements at 77 K were made with the sample mounted over a pinhole inside a cryostat with  $\text{BaF}_2$  outer windows and  $\text{CsI}$  inner windows. When the microscope was used the resolution was  $1\text{ cm}^{-1}$  but with the cryostat it was only  $4\text{ cm}^{-1}$  because of the reduction in throughput. The lower energy limit of the absorption spectra depends upon the detector used. The TGS detector used with the microscope allowed measurements to be taken down to  $\sim 500\text{ cm}^{-1}$ . The MCT detector cuts off at  $\sim 740\text{ cm}^{-1}$  but is more sensitive and was therefore used to take the 77 K spectra.

The bandgap of solid  $\text{C}_{60}$  was found by Lof *et al* (1992) to be 2.3 eV and they concluded that absorption occurring in the 1.5–2 eV range is due to Frenkel-type molecular excitons (see also Leach *et al* 1992). The fullerene crystals are opaque to the laser light used in the Raman experiments but relatively transparent to the infrared. This means that the Raman measurements only probe the crystal near the surface whereas the infrared absorption is measured through the bulk of the crystal. Effects of oxygen absorbed in the surface layer will therefore be more significant in the Raman spectra.

### 3. Experimental results

#### 3.1. Raman spectra

The Raman spectrum of the unexposed  $\text{C}_{60}$  sample in a glass tube (see section 2) was obscured by stray light but prominent features could nevertheless be observed at  $1459$  and  $1468\text{ cm}^{-1}$  above 250 K; as the temperature was lowered below 250 K the  $1459\text{ cm}^{-1}$  line disappeared and the  $1468\text{ cm}^{-1}$  line grew in intensity (figure 1). Further experiments to be described below show that the  $1459\text{ cm}^{-1}$  line is due to the highest  $A_g$  mode of pure  $\text{C}_{60}$  whereas the sharper  $1468\text{ cm}^{-1}$  line arises from parts of the crystal containing residual

molecular oxygen. The oxygen inhibits rotation of the  $C_{60}$  molecules in its vicinity giving a spectrum at room temperature similar to that observed in the pure crystal below the 250 K transition. The relative intensity of the  $A_g$  and  $H_g$  modes (figure 1) depends quite strongly on the wavelength of excitation. At room temperature, with the 457.9 nm line of an argon ion laser it is about twice as intense. However, with the 514.5 nm line of the argon ion laser it is about 15 times more intense at 280 K and about 24 times more intense at 40 K (see van Loosdrecht *et al* 1992). There is a weak resonance in the Raman spectrum when excited by laser light in the 4965 Å~4880 Å region. It is difficult, because of low intensity, to study changes in intensity and energy of the  $H_g$  modes in our unexposed  $C_{60}$  crystals at the phase transition (figure 1(b)).

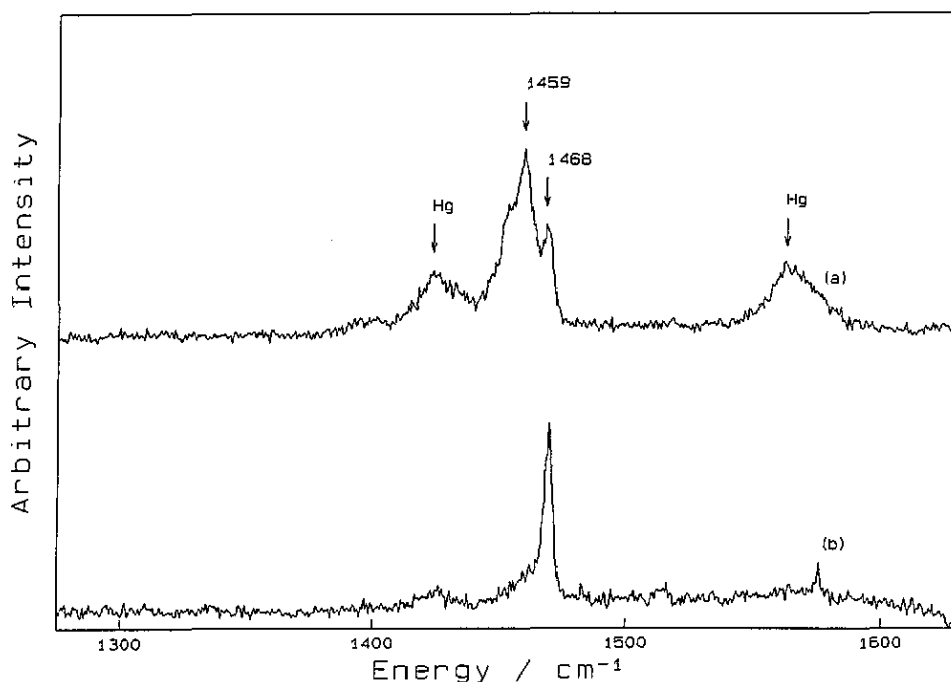


Figure 1. Raman spectra of  $C_{60}$  crystal that had not been exposed to the atmosphere, (a) 255 K and (b) 250 K.  $\lambda = 5145 \text{ \AA}$ .

The behaviour described above contrasts with that of samples that had been exposed to the atmosphere for several weeks, in that the Raman spectra of the latter change markedly with irradiation time. At room temperature the highest  $A_g$  mode occurs initially at 1468  $\text{cm}^{-1}$  but shifts to 1458  $\text{cm}^{-1}$  and the highest  $H_g$  mode occurs initially at 1575  $\text{cm}^{-1}$  but shifts to 1565  $\text{cm}^{-1}$  when exposed to 3 mW of 4880 Å light for 10 minutes; at 200 K under the same irradiation conditions this shift occurs in ~6 hours (there is no measurable shift of the  $H_g$  mode at 1425  $\text{cm}^{-1}$ ). Below 200 K no laser induced change was observed. Exposure to the laser light above 200 K also resulted in the growth of a Raman line at 1625  $\text{cm}^{-1}$  in the time scales mentioned above (figure 2). If the laser is switched off for a period of hours and the sample left undisturbed in a helium atmosphere the line shifts are

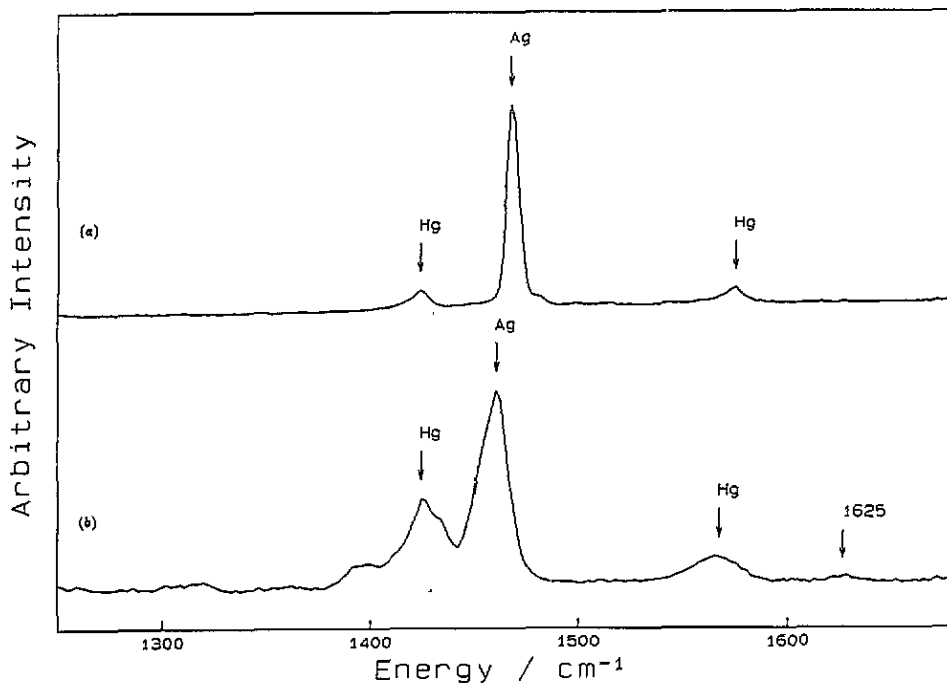


Figure 2. (a) Raman spectrum of an unsolvated single-crystal of  $C_{60}$  at 220 K with 4965 Å excitation of a previously unirradiated spot. (b) Spectrum at 220 K after being irradiated at 220 K for 6 hours with a 3 mW, point focussed, 5145 Å laser beam.

not reversed. The solvated crystals showed similar line shifts and also the growth of the mode at  $1625\text{ cm}^{-1}$ , but over longer time scales.

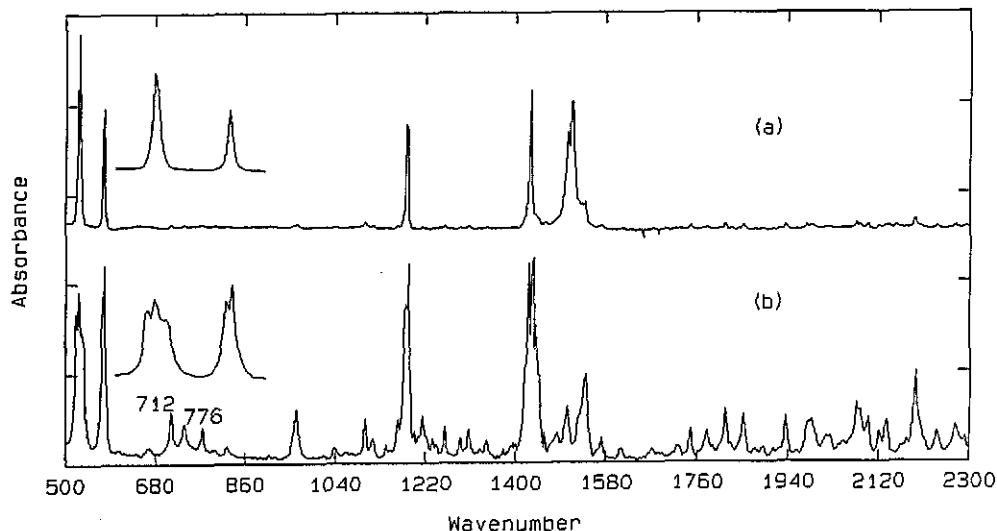
The Raman spectrum of a freshly cleaved  $ET_2C_{60}$  crystal face did not change with time. At room temperature the mode at  $1625\text{ cm}^{-1}$  is observed, the highest  $A_g$  mode is at  $1461\text{ cm}^{-1}$  and the highest  $H_g$  mode is at  $1567\text{ cm}^{-1}$ . Upon cooling below 150 K the spectra became sharper (see also Izuoka *et al* 1992) and the  $A_g$  and  $H_g$  modes shifted to  $1471\text{ cm}^{-1}$  and  $1576\text{ cm}^{-1}$  respectively; the line at  $1625\text{ cm}^{-1}$  disappeared below 150 K indicating a freezing out of rotation of  $C_{60}$  at this temperature. After the freshly cleaved crystal face had been exposed to the atmosphere for a week the room temperature Raman spectrum changed: the  $1625\text{ cm}^{-1}$  band had disappeared, the  $A_g$  mode shifted to  $1467\text{ cm}^{-1}$  whilst the  $H_g$  mode shifted to  $1573\text{ cm}^{-1}$ . After laser irradiation for a period of 12 hours at room temperature the spectrum changed back to that previously measured from the freshly cleaved surface. This reversibility is consistent with surface absorption of  $O_2$  on exposure to the atmosphere and removal of the  $O_2$  on laser irradiation.

The 4.2 K Raman spectra from all three types of  $C_{60}$  materials studied (see section 1) were very similar with only small differences in peak positions and relative intensities of the individual peaks.

### 3.2. Infrared absorption

Figure 3(a) shows the infrared absorption at room temperature of a  $CS_2$  solvated  $C_{60}$  crystal and figure 3(b) shows the absorption of a solvent-free crystal. The spectrum of the solvated

crystal shows five strong features; the four of lowest energy correspond to the  $T_{1u}$  modes of the  $C_{60}$  molecule whilst the strong absorption at  $\sim 1530\text{ cm}^{-1}$  corresponds to the infrared active asymmetrical stretch mode of  $CS_2$ , which occurs at  $1532.5\text{ cm}^{-1}$  in the gas phase (Wentink 1953). The four  $T_{1u}$  modes in the solvent-free  $C_{60}$  spectrum show fine structure (figure 3(b)) and there are many other weak features that are also present, but enhanced compared to the solvated crystal.



**Figure 3.** Infrared absorption spectrum at room temperature of (a) a single crystal of  $CS_2$  solvated  $C_{60}$  and (b) a single crystal of unsolvated  $C_{60}$ . The insets show the first two  $T_{1u}$  modes on an expanded scale.

#### 4. Discussion

The presence of enhanced infrared modes in the infrared absorption spectrum of the solvent-free crystal (figure 3) indicates that the solvated crystal is less anharmonic than the unsolvated one. Furthermore, some of the same features at  $712$  and  $776\text{ cm}^{-1}$ , for example (see figure 3), are also present in the Raman spectrum, where they are identified as  $H_g$  modes (possible origins of the other peaks are discussed by Bowmar 1993).

On symmetry grounds the  $T_{1u}$  modes of unsolvated  $C_{60}$  should not show fine structure in the FCC phase (section 1). However such structure could arise from Fermi resonances, which occur when a forbidden or combination mode lies close in energy to an allowed mode and they are mixed by anharmonicity (Herzberg 1945). The lowest energy  $T_{1u}$  infrared peak is split into three components at  $522$ ,  $526$  and  $534\text{ cm}^{-1}$  (figure 3(b)). The  $522\text{ cm}^{-1}$  mode may be an overtone of a mode at  $261\text{ cm}^{-1}$ . Similarly, the  $T_{1u}$  mode at  $576\text{ cm}^{-1}$  is split into two modes at  $574$  and  $578\text{ cm}^{-1}$  corresponding to the two fundamentals found by neutron scattering in this region (Coulombeau *et al* 1992). The  $T_{1u}$  modes at  $1183\text{ cm}^{-1}$  and  $1430\text{ cm}^{-1}$  are also split (figure 3(b)) but at these energies the resolution of the neutron data of Coulombeau *et al* (1992) is not sufficient to be helpful. This behaviour contrasts with that of thin films of  $C_{60}$  where Narasimhan *et al* (1992) observed a  $1430\text{ cm}^{-1}$  peak at



room temperature with a weak shoulder at  $1424\text{ cm}^{-1}$  in the absorption spectra of  $\sim 5500\text{ \AA}$  thick films, in contrast to the strong features at  $1426$ ,  $1434$  and  $1440\text{ cm}^{-1}$  in the single crystal. The peak at  $1430\text{ cm}^{-1}$  observed in thin films (Narasimhan *et al* 1992) gradually splits below  $245\text{ K}$  into two modes at  $1428\text{ cm}^{-1}$  and  $1431\text{ cm}^{-1}$ . Narasimhan *et al* (1992) did not observe many of the weaker features present in our spectra, suggesting that the films do not have quite the same structure as the bulk crystals. The forbidden modes in our infrared spectra become more intense at  $77\text{ K}$  relative to the four allowed  $T_{1u}$  modes, indicating increased anharmonicity at the lower temperature. However, the resolution at low temperatures was not sufficient to examine any temperature dependence of the splitting of the infrared features (see section 2).

Zhou *et al* (1992) have shown that  $C_{60}$  films, when exposed to oxygen at room temperature, take up about 5 oxygen atoms per  $C_{60}$  molecule. The chemical state of the oxygen in solid  $C_{60}$  has not been clearly established (ionic bonding is unlikely since the ionisation potential of  $C_{60}$  is  $\sim 7\text{ eV}$  (Ros n *et al* 1988), whereas the electron affinities of O and  $O_2$  are  $0.47$  and  $0.45\text{ eV}$  respectively (Weast 1983)). Nissen *et al* (1992) observed the characteristic luminescence spectrum of molecular oxygen in the near infrared. A weak sideband was seen corresponding to a vibrational mode of  $O_2$  at  $1540\text{ cm}^{-1}$  (verified by exposing a sample to  $^{18}O_2$  and observing the isotopic shift). This highly structured luminescence spectrum contains phonon replicas corresponding to  $C_{60}$  intramolecular vibrational modes and the corresponding bonding of the molecule (probably of the van de Waals type in an octahedral interstitial site) is strong enough to inhibit rotation of  $C_{60}$  at room temperature. Arai *et al* (1992) have shown that absorption of oxygen by crystals of  $C_{60}$  at room temperature increases the resistivity by four orders of magnitude and they conclude that molecular oxygen acts as a compensating acceptor. They have also shown that the molecular oxygen is desorbed above  $300\text{ }^\circ\text{C}$  in vacuum and that the cycle of absorption and desorption is repeatable.

In order to explain the behaviour of the highest  $A_g$  and  $H_g$  modes and the  $1625\text{ cm}^{-1}$  line in the Raman spectrum of the unsolvated crystal described above we propose that laser irradiation above  $200\text{ K}$  removes molecular oxygen close to the crystal surface (see below) and consequently the transition from the FCC to the SC phase does not occur down to  $200\text{ K}$  in this localized region (compare van Loosdrecht *et al* (1992)). Our results are consistent with those of Duclos *et al* (1991), who showed that upon exposure of thin films of  $C_{60}$  to oxygen at room temperature the highest  $A_g$  mode shifted from  $1458$  to  $1470\text{ cm}^{-1}$ , the highest  $H_g$  mode shifted from  $1565$  to  $1575\text{ cm}^{-1}$  and an additional mode at  $1625\text{ cm}^{-1}$  in the unexposed film disappeared; the shift of the  $A_g$  mode was reversed by prolonged laser irradiation.

The origin of the  $1625\text{ cm}^{-1}$  Raman mode (relatively intense using  $457.9\text{ nm}$  excitation but much weaker with  $514.5\text{ nm}$  excitation), observed with both the green and blue laser lines, is not clear. However, weak features observed with the green laser lines, that could be assigned to combinations and overtones, were not observed with the blue laser lines. This suggests that the  $1625\text{ cm}^{-1}$  mode may be a fundamental mode made Raman active in all the materials studied by the onset of rotational perturbation. However, existing calculations are not sufficiently accurate to pinpoint the nature of the mode (see e.g. Jishi *et al* 1992).

Our Raman spectra (resolution  $\sim 1\text{ cm}^{-1}$ ) of single crystals show no evidence of structure associated with  $H_g$  modes. The only polarized features (i.e. those absent when the scattered light in the quasi-back-scattering configuration is filtered by polaroid crossed with the polarization of the incident light) correspond to the  $A_g$  modes of the isolated molecule (Bowmar 1993, Dresselhaus *et al* 1992). On the other hand, the Raman spectra show many other weak peaks and shoulders besides the  $H_g$  and  $A_g$  modes, but since these features

are also observed in the Raman spectra of CS<sub>2</sub> solvated crystals and ET<sub>2</sub>C<sub>60</sub> crystals and in the neutron data of Coulombeau *et al* (1992) it is clear that they are combinations and fundamentals of the C<sub>60</sub> molecule.

van Loosdrecht *et al* (1992) observed larger linewidths in the FCC phase of the uncontaminated crystal when compared with the SC phase, corresponding to a decrease in the phonon lifetime and they associated this with the onset of rotation (the rotational correlation time is 9 ps (section 1)). Figure 2(b) shows a similar increase in linewidth upon removal of oxygen (compare figure 2(a)) and our experiments indicate that the absorbed oxygen inhibits free rotation of the C<sub>60</sub> molecules up to 293 K.

No phase change is observed between 250 K and 200 K in the very small region of the unsolvated crystal cleared of oxygen by the laser, possibly due to the presence of oxygen in the surrounding material. The region of the crystal cleared of oxygen retains the intermolecular separation of the FCC phase to below the 250 K bulk transition temperature and the C<sub>60</sub> molecules remain spinning in the localized oxygen-free region down to 200 K. The period of laser irradiation required to remove the oxygen was found to increase as the temperature was decreased. This suggests that the 200 K lower limit corresponds to the rate of oxygen removal becoming too slow to be observed. This lower temperature limit was also observed with the solvated crystals.

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