

Raman and infrared determination of vibrational fundamentals of single-crystal C₆₀ and derivatives and of C₇₀

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 3161

(<http://iopscience.iop.org/0953-8984/6/17/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 12/05/2010 at 18:15

Please note that [terms and conditions apply](#).

Raman and infrared determination of vibrational fundamentals of single-crystal C₆₀ and derivatives and of C₇₀

P Bowmar†, W Hayes †, M Kurmoo†‡, P A Pattenden†, M A Green‡, P Day‡ and K Kikuchi§

† Department of Physics, Clarendon Laboratory, Oxford University, Parks Road, Oxford OX1 3PU, UK

‡ The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK

§ Department of Chemistry, Tokyo Metropolitan University, Hachoji, Tokyo 192-03, Japan

Received 27 September 1993, in final form 28 February 1994

Abstract. We describe results of Raman and infrared (IR) studies of single crystals of pure C₆₀, CS₂ solvated C₆₀ (C₆₀1.5CS₂), (BEDT-TTF)₂ C₆₀ (BEDT-TTF or ET is bis(ethylenedithio)tetrathiafulvalene) and C₇₀. We find that changing the crystalline environment of C₆₀ has little effect upon the vibrational frequencies of the intramolecular vibrations but has some effect on relative intensities of peaks. By comparing our IR and Raman spectra using the published inelastic neutron scattering and surface enhanced Raman data we have been able to identify the complete set of 46 fundamental intramolecular vibrational frequencies of C₆₀ and 64 of the 122 fundamentals of C₇₀. Theoretical calculations for C₆₀ are not accurate enough to completely assign the symmetries of the identified fundamentals. We comment on effects of oxygen and laser power on the Raman spectrum of C₆₀.

1. Introduction

Recently Raman, surface enhanced Raman scattering (SERS), and inelastic neutron scattering (INS) studies of the intramolecular vibrations of C₆₀ and C₇₀ have been published (van Loosdrecht *et al* 1992a, 1993, Dong *et al* 1993, Chandrabhas *et al* 1993, Liu *et al* 1992, Coulombeau *et al* 1992, Christides *et al* 1993). However, examination of the published Raman spectra reveals several discrepancies with the published neutron data. We have therefore studied C₆₀ molecules in a number of different crystalline environments. We report here Raman and infrared (IR) spectra of single crystals of unsolvated C₆₀, CS₂ solvated C₆₀ (C₆₀1.5CS₂), (BEDT-TTF)₂C₆₀ (BEDT-TTF or ET is bis(ethylenedithio)tetrathiafulvalene) and C₇₀. We have previously discussed the vibrational modes and the selection rules for Raman and infrared spectra of C₆₀ molecules (Bowmar *et al* 1993); there are 46 fundamentals. Isolated C₇₀ has D_{5h} symmetry and the vibrations have the following representations (Raghavachari and Rohlfing 1991):

$$\Gamma = 10A_2'' + 21E_1' + 12A_1' + 22E_2' + 19E_2'' + 9A_2' + 9A_1'' + 20E_2''$$

giving 122 fundamentals. The A₂'' and E₁' modes are IR active and the A₁', E₂' and E₁'' modes are Raman active. The degeneracy of the intramolecular vibrations of C₇₀ cannot be determined by INS as unambiguously as with C₆₀ because there are five inequivalent carbon atoms in the C₇₀ molecule and the scattering cross section is therefore dependent upon the eigenvector of each mode; this is in contrast to C₆₀, which has 60 equivalent carbon atoms and a cross section independent of the eigenvector.

Unsolvated C_{70} grown by sublimation has a hexagonal close packed (HCP) structure with a small admixture of a face centred cubic (FCC) phase and a second HCP phase. After annealing at 573 K (see below) for 17 days the structure becomes predominantly FCC (Green *et al* 1992). Chandrabhas *et al* (1993) showed that the Raman linewidths and peak positions varied smoothly with temperature and concluded that the C_{70} molecules are totally orientationally disordered above 330 K, disordered about the long axis of the molecule between 330 K and 270 K and orientationally ordered below 270 K (Maniwa *et al* (1993) find an orientational phase transition at 280 K).

The aim of this paper is to distinguish fundamental vibrations from combinations and overtones in the complicated IR and Raman vibrational spectra of C_{60} and C_{70} . We also discuss effects of oxygen and laser power on the Raman spectrum of C_{60} (see subsection 4.3).

2. Experimental details

The preparation by sublimation of single crystals of C_{60} and derivatives has previously been described (Bowmar *et al* 1993). Single crystals of C_{70} were also prepared by sublimation and some of these crystals were then annealed at 573 K under a vacuum of 10^{-1} Torr (see section 1). These C_{70} crystals are referred to below as unannealed and annealed (Green *et al* 1992). Details of the Raman and IR equipment used have been previously given (Bowmar *et al* 1993). The resolution was 0.7 cm^{-1} . The laser power density was always less than 0.5 W cm^{-2} , to minimize possible photochemical effects (see subsection 4.3), and there was a consequent penalty in signal to noise ratio (see section 3).

3. Results

The infrared absorption at room temperature of a CS_2 solvated C_{60} and a solvent free crystal have already been described (Bowmar *et al* 1993) and the measured peaks are listed in table 1. Figure 1 shows the IR absorption spectrum of an unannealed C_{70} crystal at room temperature. No significant difference was observed compared to the annealed crystal. Table 2 lists the absorption peaks.

The effects of exposure to air and of temperature upon the Raman spectrum of crystals of C_{60} and derivatives have been previously discussed (Bowmar *et al* 1993). The room temperature Raman spectra measured from oxygen-free solvated C_{60} , unsolvated C_{60} and ET_2C_{60} and the corresponding spectra at 4 K are shown in figure 2. Figure 3(a) gives the Raman spectrum of C_{60} at 4 K with increased amplification below $\sim 1400\text{ cm}^{-1}$, showing weaker structure (the presence of oxygen in the crystals affects the Raman spectrum at room temperature but not at 4 K). The Raman spectra from all three types of C_{60} material studied (see section 1) were very similar with only small differences in energies and relative intensities of the individual peaks. There was a weak resonance with the green Ar^+ ion laser lines with both the solvated and unsolvated C_{60} crystals. The Raman spectrum of ET_2C_{60} did not vary significantly with exciting laser frequency over the Ar^+ range. However the relative intensities of peaks present in the Raman spectrum of the unsolvated C_{60} crystal changed considerably when excited by the 4579 \AA Ar^+ line rather than the 5145 \AA line and the effect was helpful in distinguishing between combinations and fundamentals. No Raman features originating from CS_2 or ET were observed for any of our crystals (see Wentink 1958, Kozlov *et al* 1987).

Figure 3(b) shows the Raman spectrum from the annealed C_{70} crystal at 4 K. The Raman spectrum did not vary significantly with temperature or with duration of laser irradiation.

Vibrational frequencies (cm⁻¹) of C₆₀ and its derivatives

| Raman C ₆₀ , C ₇₀ , C ₇₆ | Raman E1-C ₆₀ 4.2R | Raman C ₆₀ 4.2R | IR C ₆₀ 293K | IR C ₆₀ 293K | IR C ₆₀ 293K | IR C ₆₀ 293K | IR C ₆₀ 293K | Assignment |
|--|-------------------------------------|----------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-----------------------|
| 271* | 268 | 273* | 271 | 273 | 271 | 273 | 271 | g ₁ |
| 355 | 353 | 353 | 344 | 342 | 344 | 342 | 344 | g ₃ |
| 429* | 428 | 429* | 432 | 429* | 432 | 429* | 432 | g ₆ |
| 484 | 484* | 484* | 488 | 488 | 488 | 488 | 488 | g ₈ |
| 496 | 494 | 493* | 488 | 490* | 488 | 490* | 488 | g _{9(a)} |
| 528 | 530 | 529 | 526 | 527 | 526 | 527 | 526 | g ₁₁ |
| 534 | 534 | 536 | 534 | 534 | 534 | 534 | 534 | g ₁₁ |
| 568 | 567 | 567 | 565 | 567 | 565 | 567 | 565 | g ₁₂ |
| 578 | 580 | 578 | 576 | 578 | 576 | 578 | 576 | g ₁₃ |
| 669 | 669 | 673 | 673 | 669 | 673 | 669 | 673 | g ₁₄ |
| 708 | 709 | 708* | 715 | 709* | 712 | 709* | 712 | g ₁₅ |
| 726 | 741 | 726 | 726 | 726 | 740 | 726 | 740 | g ₁₆ |
| 757 | 756 | 755* | 755 | 755* | 756 | 755* | 756 | g ₁₈ |
| 773 | 773 | 773* | 776* | 776* | 776 | 776* | 776 | g ₁₉ |
| | | 792 | | 796 | | 796 | | 1+11 or 1+10 |
| | | | 813 | | | | 826 | g ₂₀ |
| | | | | | | | | 3+8 |
| 860 | 860 | 860 | 860 | 860 | 860 | 860 | 860 | g ₂₁ |
| 960 | 956 | 956 | 956 | 956 | 962 | 956 | 962 | g ₂₂ |
| 975 | 975 | 971 | 971 | 971 | 964 | 971 | 964 | g ₂₃ |
| | | 980 | | 983 | | 983 | | g ₂₄ |
| 1056 | 1041 | 1016 | 1016 | 1042 | 1040 | 1042 | 1040 | 18+1 or 8+11 |
| 1078 | 1078 | 1080* | 1078 | 1078 | 1078 | 1078 | 1078 | 8+11 or 14+11 or 19+9 |
| 1100 | 1099 | 1101* | 1100 | 1096 | 1100 | 1096 | 1100 | g ₂₅ |
| 1138 | 1138 | 1138 | 1142 | 1139 | 1142 | 1139 | 1142 | 5/6+7 |
| | | | 1166 | 1166 | 1166 | 1166 | 1166 | g ₂₆ |
| | | | 1173 | 1173 | 1173 | 1173 | 1173 | g ₂₇ |
| 1185 | 1184 | 1187 | 1186 | 1186 | 1186 | 1186 | 1186 | g ₂₈ |
| | | | | | | | | 7+12 or 21+2 or 7+12 |
| 1202 | 1202 | 1202 | 1196 | 1196 | 1198 | 1196 | 1198 | 8+15 or 42 |

Table 1. Vibrational frequencies (cm⁻¹) of C₆₀ and its derivatives. @ denotes a fundamental.

| Raman C ₆₀ , C ₇₀ | Raman E1-C ₆₀ 4.2R | Raman C ₆₀ 4.2R | IR C ₆₀ 293K | IR C ₆₀ 293K | IR C ₆₀ 293K | IR C ₆₀ 293K | IR C ₆₀ 293K | Assignment |
|---|-------------------------------------|----------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|------------------------------------|
| 1352 | | 1251* | 1246 | 1246 | 1246 | 1246 | 1246 | 15+11 or 5/6+21 |
| | | 1261 | 1261 | 1261 | 1261 | 1261 | 1261 | @(H _g)g ₃₀ |
| | | 1272 | 1272 | 1272 | 1272 | 1272 | 1272 | 16+11 |
| | | 1285 | 1285 | 1285 | 1285 | 1285 | 1285 | 18+10 |
| | | 1290 | 1290 | 1290 | 1290 | 1290 | 1290 | 15+13 or 18+11 |
| | | 1302 | 1302 | 1302 | 1302 | 1302 | 1302 | @g ₃₁ |
| | | 1315 | 1315 | 1315 | 1315 | 1315 | 1315 | @g ₃₂ |
| | | 1344 | 1344 | 1344 | 1344 | 1344 | 1344 | 17+12 or 16+11 |
| 1347 | | 1356 | 1356 | 1356 | 1356 | 1356 | 1356 | @g ₃₃ |
| | | 1362 | 1362 | 1362 | 1362 | 1362 | 1362 | @g ₃₄ |
| | | 1376 | 1376 | 1376 | 1376 | 1376 | 1376 | 1+25 |
| | | 1395 | 1395 | 1395 | 1395 | 1395 | 1395 | 2+25 |
| 1418 | | 1418 | 1418 | 1418 | 1418 | 1418 | 1418 | 15+15 or 13+21 |
| 1425* | | 1425* | 1425* | 1425* | 1425* | 1425* | 1425* | @(H _g)g ₃₅ |
| | | 1454 | 1454 | 1454 | 1454 | 1454 | 1454 | @(T _{1u})g ₃₇ |
| | | 1460* | 1460* | 1460* | 1460* | 1460* | 1460* | @g ₃₈ |
| | | 1470 | 1470 | 1470 | 1470 | 1470 | 1470 | @(G _g)g ₃₉ |
| | | 1481 | 1481 | 1481 | 1481 | 1481 | 1481 | 18+15 |
| | | 1497 | 1497 | 1497 | 1497 | 1497 | 1497 | 17+17 or 16+18 |
| 1500 | | 1500 | 1500 | 1500 | 1500 | 1500 | 1500 | @g ₄₀ |
| | | 1520 | 1520 | 1520 | 1520 | 1520 | 1520 | 16+19 |
| | | 1539 | 1539 | 1539 | 1539 | 1539 | 1539 | @g ₄₁ |
| | | 1544-8 | 1544-8 | 1544-8 | 1544-8 | 1544-8 | 1544-8 | 25+7 |
| | | 1554+7 | 1554+7 | 1554+7 | 1554+7 | 1554+7 | 1554+7 | @g ₄₂ |
| | | 1572 | 1572 | 1572 | 1572 | 1572 | 1572 | 19+19 |
| 1576* | | 1576* | 1576* | 1576* | 1576* | 1576* | 1576* | 17+20 |
| | | 1584 | 1584 | 1584 | 1584 | 1584 | 1584 | 24+9 |
| | | 1610-4 | 1610-4 | 1610-4 | 1610-4 | 1610-4 | 1610-4 | @(H _g)g ₄₃ |
| | | 1625* | 1625* | 1625* | 1625* | 1625* | 1625* | @g ₄₄ |

@ denotes a fundamental

IR active combinations above 1625cm⁻¹.

1628, 1648, 1656, 1672, 1684, 1692, 1722, 1748, 1760, 1792, 1816, 1838, 1852, 1876, 1892, 1912, 1924, 1936, 1980, 1984, 2016, 2024, 2076, 2120, 2136, 2176, 2192, 2236, 2272, 2282, 2312, 2332, 2360, 2388, 2420, 2456, 2504, 2528, 2560, 2604, 2628, 2704, 2736, 2812, 2840, 2852, 2888, 2912, 2948, 3004 and 3072

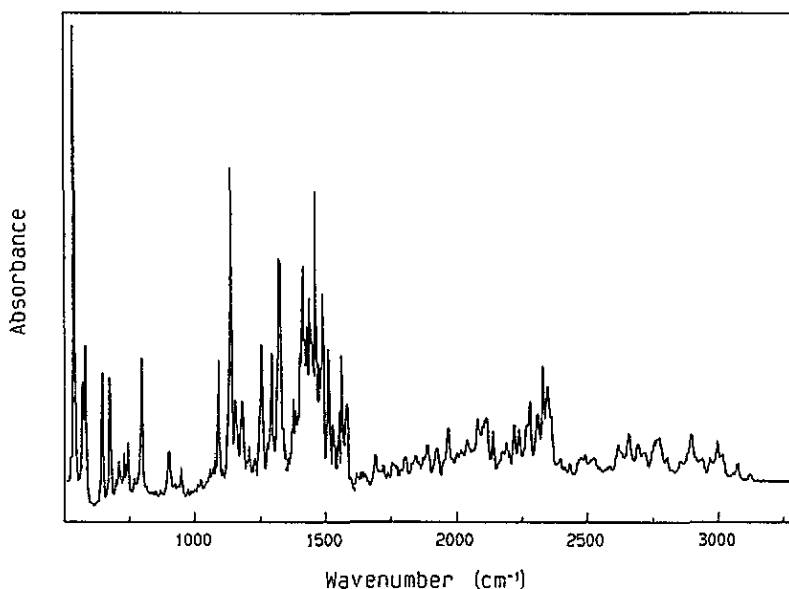


Figure 1. The IR absorption spectrum of an unannealed single crystal of C_{70} at 293 K.

The intensity of the Raman spectrum increased on changing the laser wavelength over the range 4579–5145 Å but did not go through a resonance. Raman spectra from the annealed C_{70} crystals were very similar to those from unannealed crystals but the spectra were slightly sharper. The peak positions are listed in table 2.

4. Discussion

4.1. C_{60} and its derivatives

The infrared absorption spectra of both solvated and unsolvated C_{60} extend to 3072 cm^{-1} , embracing two-phonon absorption. No features were observed above this range, indicating that three-phonon absorption is weak. Apart from the CS_2 modes discussed previously (Bowmar *et al* 1993), the IR absorption peaks measured from solvated C_{60} crystals were the same as those measured from unsolvated C_{60} (apart from a few weak missing peaks; see Bowmar *et al* (1993) for a discussion).

Van Loosdrecht *et al* (1992a) showed that some Raman vibrational lines shift discontinuously to higher energy and become narrower on cooling through the FCC-SC phase transition at 252 K. A similar behaviour was observed for all of the C_{60} derivatives studied by us (figure 2) and is associated with the hindrance of rotation of the C_{60} molecules (Bowmar *et al* 1993). It is interesting to note that the infrared peak observed at 574 cm^{-1} at room temperature softens to 567 cm^{-1} at 4 K in the Raman spectra of all three types of C_{60} material studied. A similar softening at low temperatures can be seen for many modes in table 1 (see also van Loosdrecht *et al* (1992a)). This is an interesting result since most materials exhibit a hardening of vibrations with decreasing temperature.

Fundamentals were distinguished from combinations and overtones by a detailed comparison of Raman, IR and INS spectra. Peaks in the Raman scattering spectrum observed off resonance were assigned to fundamentals (these are marked with an asterisk in table 1).

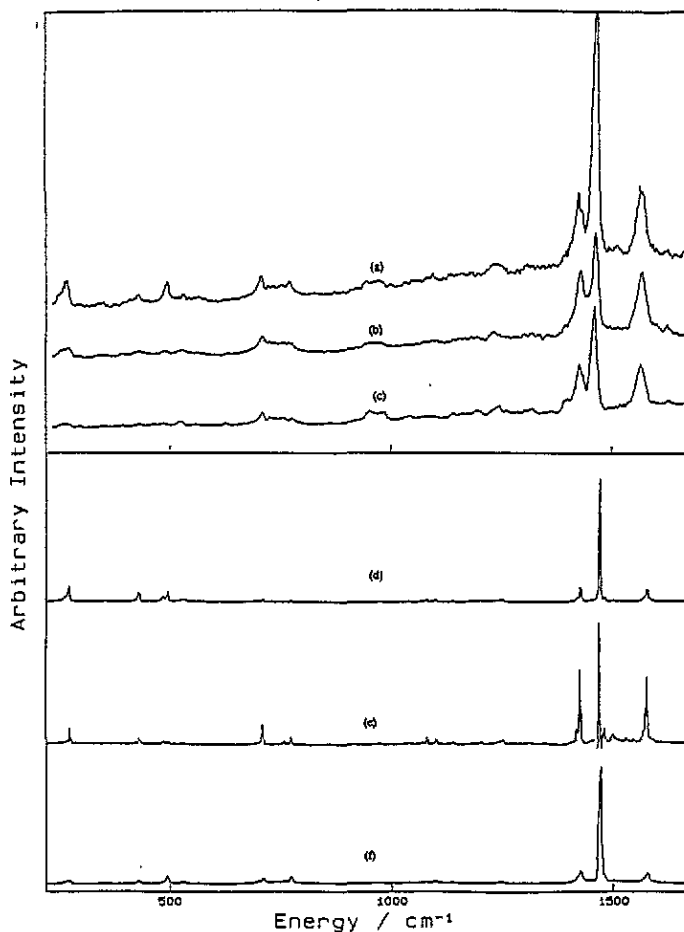


Figure 2. Raman spectra of (a) CS₂ solvated C₆₀, (b) unsolvated C₆₀ and (c) ET₂C₆₀ excited by a 5145 Å Ar⁺ ion laser at 293 K. (a) and (b) were measured after the Raman spectra had ceased to change with time due to the removal of molecular oxygen. (c) was measured from a freshly cleaved surface of ET₂C₆₀. (d), (e) and (f) were measured at 4 K from CS₂ solvated C₆₀, unsolvated C₆₀ and ET₂C₆₀ respectively.

The extra peaks observed in resonance may be fundamentals, combinations or overtones. The allowed Raman modes (symmetry h_g and a_g) could be assigned on intensity grounds, with the a_g and h_g modes being distinguishable because the a_g Raman tensor is diagonal. Two peaks of similar intensity were observed at 1100 and 1080 cm⁻¹. The 1100 cm⁻¹ mode can be assigned as h_g by comparison with solution spectra (Chase *et al* 1992). Four strong IR allowed modes were observed from unsolvated C₆₀ and these were assigned to T_{1u} modes (these peaks exhibited partly resolved structure and we have previously attributed this to Fermi resonances (Bowmar *et al* 1993); the structure was not resolved in the less anharmonic C₆₀1.5CS₂).

The INS data of Coulombeau *et al* (1992) can be used to identify the fundamental vibrations in the IR and Raman spectra of C₆₀ below 1000 cm⁻¹ (see table 1). Those peaks that do not lie close to a fundamental in the INS spectra can be accounted for by combinations or overtones of fundamentals (to within the experimental accuracy of ~2 cm⁻¹). We did

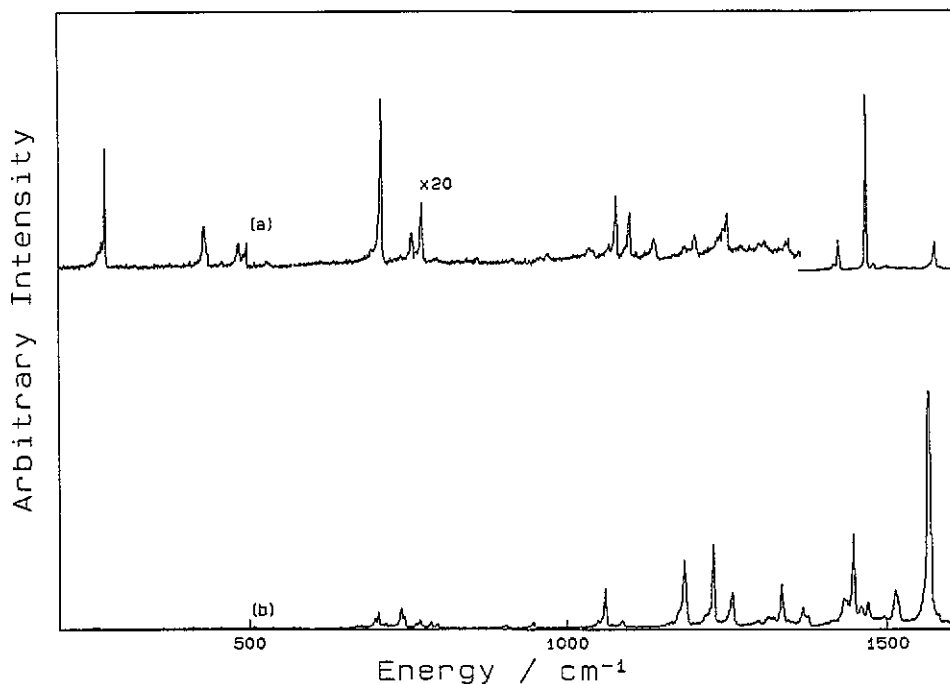


Figure 3. (a) The Raman spectrum of unsolvated C_{60} at 4 K, with the low-energy region enlarged. (b) The Raman spectrum of annealed C_{70} at 4 K.

not identify crystal field splittings of the fundamentals from this detailed comparison (see table 1). This is consistent with only minor differences being observed between the positions of the main Raman and IR peaks of C_{60} molecules in the different crystalline environments of our C_{60} derivatives (see table 1 and also Matus and Kuzmany (1993) for a discussion of crystal field effects in crystalline C_{60} , not observable in our spectra because of lower signal to noise ratio (see section 2)). Clear changes in relative intensities of Raman peaks are however observed for different derivatives of C_{60} (see figure 2). When assigning peaks to combinations or overtones we bear in mind that effects of inversion symmetry are relaxed in both the IR and Raman spectra (Bowmar *et al* 1993).

Our analysis was extended to the region between 1000 and 1625 cm^{-1} by comparing the weak IR peaks and those peaks observed only in resonance Raman spectra with combinations and overtones of the fundamentals below 1000 cm^{-1} ; 45 fundamentals were found, leaving one fundamental unidentified (see section 1). The peaks in the IR absorption spectrum between 1625 and 3072 cm^{-1} correspond to combinations and overtones only and all could be accounted for with the exception of two peaks at 2912 and 3072 cm^{-1} . The remaining fundamental may be sought by subtracting all of the 45 fundamentals from the two peaks above and looking for energies that occur twice. This suggests that the remaining fundamental is at 1488 cm^{-1} , absent from our Raman spectra. However, a line close to this frequency (at 1480 cm^{-1}) has been observed in SERS measurements (Liu *et al* 1992) and with this addition all 46 fundamentals are assigned.

Calculations of the vibrational spectrum of C_{60} are not accurate. It can be shown that by considering only nearest-neighbour interactions no choice of the bond stretching force constants of the bond lying along pentagon-hexagon or hexagon-hexagon edges can reproduce the frequencies of the two a_g vibrational modes (Jishi *et al* 1992). Jishi

et al (1992) also considered interactions up to third-nearest neighbours, fitting the force constants to the Raman active modes observed by experiment, but the inaccuracies of the calculations do not make it possible for us to assign symmetry representations to most of the fundamentals with any confidence (see table 1). The INS data of Coulombeau *et al* (1992) give the degeneracy of the modes below 1000 cm^{-1} , helping to assign symmetries in this region (see table 1).

We should point out that some of our assignments do not agree with those of van Loosdrecht *et al* (1993a) or Dong *et al* (1993). Van Loosdrecht *et al* (1993a) analysed their data by assuming that crystal fields make only even modes Raman active. The modes were then assigned by comparison with results of a calculation by Negri *et al* (1988) and by attributing any extra modes to crystal field splitting of degenerate modes. In contrast, we have indicated above that parity rules are not strictly obeyed in the Raman spectra and we have suggested that published calculations are not sufficiently accurate to give a reliable guide in interpreting spectra.

Dong *et al* (1993) observed many Raman peaks above 1625 cm^{-1} from a thin film. These peaks were not observed from single crystals by either van Loosdrecht *et al* (1993a) or ourselves. This may be a consequence of resonance conditions in thin films different from those found in single crystals. Matus *et al* (1991) observed a sharp resonance from thin films, whilst we find a broader resonance from our single-crystal samples. Dong *et al* (1993) attempted to derive all of the fundamentals by producing a set of frequencies and symmetry assignments that could account for the higher-order Raman peaks, using the calculations of Jishi *et al* (1992) as a guide, but few of these calculated frequencies lie close to our data. Furthermore, the INS data of Coulombeau *et al* (1992) show that many of these frequencies are incorrectly assigned.

4.2. C_{70} crystals

Table 2 shows our observed IR and Raman peaks for C_{70} together with results of SERS measurements of Liu *et al* (1992) and the INS data of Christides *et al* (1993). The data were analysed in a similar manner to those for C_{60} . However, the degeneracies of the vibrational modes cannot be simply found from INS (see section 1). The Raman and IR data agree with the low-energy range of the neutron data but above 682 cm^{-1} the neutron data are generally of little use because of poor resolution (except for well resolved modes at 899 and 955 cm^{-1}). However, the number of modes assigned by neutron scattering disagrees with our data in regions with a large number of closely spaced modes, e.g. at $\sim 530\text{ cm}^{-1}$ with C_{70} (table 2) and $\sim 750\text{ cm}^{-1}$ with C_{60} (table 1).

The large number of observed C_{70} modes makes the use of combinations and overtones to identify weakly allowed fundamentals very limited; in fact only one peak at 1384 cm^{-1} was identified by considering combinations and overtones and so table 1 does not list the possible combinations. Intense peaks in the Raman and IR spectra are tentatively assigned to fundamentals.

The Raman selection rules are relaxed with SERS but combinations and overtones are not enhanced (Otto 1984). Table 2 shows a comparison of the SERS data of Liu *et al* (1992) with our data and it can be seen that the modes are not shifted significantly. This is not the case for C_{60} : the data of Akers *et al* (1992) exhibit shifts of order 20 cm^{-1} from the Raman spectra. We therefore used the SERS data to help with the analysis of our C_{70} spectra and 64 fundamentals were identified. Above 1630 cm^{-1} six peaks could not be accounted for by combinations. We resolve many more Raman peaks than Chandrabhas *et al* (1993) but fewer than van Loosdrecht *et al* (1993b). If we compare the Raman spectrum of van Loosdrecht *et al* (1993b) with ours and with the neutron scattering data of Christides *et al*

(1993) we find extra Raman peaks in the low-energy region ($<600\text{ cm}^{-1}$) of the spectrum of van Loosdrecht *et al* (1993b) that have no counterpart in the INS spectrum and cannot be assigned to combinations or overtones. We observed our significant difference between spectra from annealed and unannealed crystals (see table 2) and our data are consistent with the resolved regions of the INS spectra.

4.3. Effects of oxygen and laser power on Raman spectra of C₆₀

Van Loosdrecht *et al* (1992a) showed using an oxygen-free single crystal of C₆₀ that an a_g mode, for example, shifts in a first-order way from 1459 cm^{-1} to 1468 cm^{-1} and narrows on cooling through the FCC-SC phase transition at $\sim 252\text{ K}$ (other lines also shift and narrow). Bowmar *et al* (1993) showed using low laser power ($<1\text{ W cm}^{-2}$) that a crystal containing some oxygen showed a_g peaks at 1459 and 1468 cm^{-1} at 255 K but on cooling to 250 K only the 1468 cm^{-1} peak was found. They suggested that oxygen hindered rotation of the C₆₀ molecule in the FCC phase, producing an effect similar to that of the FCC-SC phase change. This effect of oxygen on the dynamics of C₆₀ was directly observed subsequently by Belahmer *et al* (1993) using high-resolution nuclear magnetic resonance (NMR). They showed that association of C₆₀ with even a single oxygen molecule shifted ¹³C NMR to lower magnetic field, possibly due to charge transfer, and strongly hindered the C₆₀ rotation (see also Assink *et al* (1992)). Van Loosdrecht *et al* (1992b, 1993a) find that with excitation intensities greater than 40 W cm^{-2} at 40 K the 1468 cm^{-1} mode decreases in intensity and is replaced by structure on the low-energy side. For laser power greater than 300 W cm^{-2} the 1468 cm^{-1} mode has gone and is replaced by a broad band peaking at 1459 cm^{-1} . They suggest that the 1468 cm^{-1} mode is associated with C₆₀ in a triplet state (but see van Loosdrecht *et al* (1992a)). However, explanation of the results of Bowmar *et al* (1993) on this assumption would require a very large increase in triplet population on warming through the SC-FCC phase transition and there is at present no experimental evidence that this occurs (on the contrary, see Pilcher *et al* (1991) and Lane *et al* (1992)). A possible alternative explanation is that the a_g mode, which involves tangential motion of carbon atoms on the C₆₀ surface is particularly sensitive to charge relaxation (see e.g. Haddon *et al* (1991), which may be a consequence of the FCC-SC phase change, or to van der Waals bonding with molecular oxygen in an interstitial site (Bowmar *et al* 1993). It would be interesting to study effects of intense optical excitation on the lattice dynamics of C₆₀ using high-resolution NMR.

Recent authors have described changes in the structure of C₆₀ films caused by laser irradiation (Zhou *et al* 1992, Rao *et al* 1993). They find evidence for irreversible photoinduced polymerization for incident laser power levels greater than 5 W cm^{-2} at both 5145 and 4880 \AA (see section 2), resulting in a shift of the a_g pinch mode from 1469 to 1460 cm^{-1} at room temperature; they suggest that the 1469 cm^{-1} line is characteristic of oxygen-free FCC C₆₀. On the other hand, in a study of effects of temperatures up to 400 K and also of laser power on the Raman spectra of single-crystal C₆₀ Hamanaka *et al* (1993) found that the a_g pinch mode occurred at 1460 cm^{-1} at room temperature using low laser power (0.4 W cm^{-2} at 4880 \AA). However, as the power was increased beyond 55 W cm^{-2} the 1460 cm^{-1} peak was replaced by a peak at 1465 cm^{-1} and the effect was reversible as the laser power was reduced; comparison with effects of heating the crystal up to 400 K suggested that the changes produced by increasing laser power were due to heat. They found no evidence for polymerization of their crystals at laser power levels of up to 80 W cm^{-2} . They also found, in agreement with van Loosdrecht *et al* (1992a) and Bowmar *et al* (1993), that on cooling below the FCC-SC phase transition at $\sim 250\text{ K}$ the 1460 cm^{-1} a_g mode is replaced by a sharper peak at 1468 cm^{-1} (see above). It is apparent that at the

present time there is confusion in the literature about some aspects of Raman scattering of C₆₀, possibly contributed to by variable quality of the material studied (for example, use of films rather than crystals and the presence or otherwise of oxygen (see above)).

References

- Akers K L, Cousins L M and Moskovits M 1992 *Chem. Phys. Lett.* **180** 614
- Assink R A, Schriber J E, Loy D A, Morosin B and Carlson G A 1992 *J. Mater. Res.* **7** 2136
- Belahmer Z, Bernier P, Firllej L, Lambert J M and Ribet M 1993 *Phys. Rev. B* **47** 15 980
- Bowmar P, Kurmoo M, Green M A, Pratt F L, Hayes W, Day P and Kikuchi K 1993 *J. Phys.: Condens. Matter* **5** 2739
- Chandrabhas N, Jayaram K, Muthu D V S and Sood A K 1993 *Phys. Rev. B* **47** 10 963
- Chase B, Herron N and Holler E 1992 *J. Phys. Chem.* **96** 4262
- Christides C, Nikolaev A V, Dennis T J S, Prassides K, Negri F, Orlandi G and Zerbetto F 1992 *J. Phys. Chem.* **97** 3641
- Coulombeau C, Jobic H, Bernier P, Fabre C, Schütz D and Rassat A 1992 *J. Phys. Chem.* **96** 22
- Dong Z-H, Zhou P, Holden J M, Eklund P C, Dresselhaus M S and Dresselhaus G 1993 *Phys. Rev. B* **48** 2862
- Green M A, Kurmoo M, Day P and Kikuchi K 1992 personal communication
- Haddon R C, Hebard A F, Rosseinsky M J, Murphy D W, Duclos S J, Lyons K B, Miller B, Rosamiila J M, Fleming R M, Kortan A R, Glarum S H, Makhija A V, Muller A J, Eick R H, Zahurak S M, Tycko R, Dabbagh G and Thiel F A 1991 *Nature* **350** 600
- Hamanaka Y, Nakashima S, Hangyo M, Shinohara H and Saito Y 1993 *Phys. Rev. B* **48** 8510
- Jishi R A, Mirie R M and Dresselhaus M S 1992 *Phys. Rev. B* **45** 13 685
- Kozlov M E, Pokhodnia K I and Yurchenko A A 1987 *Spectrochim. Acta* **43** 323
- Lane P A, Swanson L S, Ni Q-X, Shinar J, Engel J P, Barton T J and Jones L 1992 *Phys. Rev. Lett.* **68** 887
- Liu J, Zhao T, Mo Y, Li T, Liu Y, Zhu K, Li Y, Yao Y, Yang D, Wang X and Zhu D 1992 *Solid State Commun.* **81** 757
- Maniwa Y, Ohi A, Mizoguchi K, Kume K, Kikuchi K, Saito K, Ikemoto I, Suzuki S and Achiba Y 1993 *J. Phys. Soc. Japan* **62** 1131
- Matus M and Kuzmany H 1993 *Appl. Phys. A* **56** 241
- Matus M, Kuzmany H and Krätschmer 1991 *Solid State Commun.* **80** 839
- Negri F, Orlandi G and Zerbetto F 1988 *Chem. Phys. Lett.* **144** 31
- Otto A 1984 *Light Scattering in Solids IV* (Berlin: Springer)
- Pichler K, Graham S, Gelsen O M, Friend R H, Romanow W J, McCauley J P Jr, Coustel N, Fischer J E and Smith A B III 1991 *J. Phys.: Condens. Matter* **3** 9259
- Raghavachari K and Rohlfling C M 1991 *J. Phys. Chem.* **95** 5768
- Rao A M, Zhou P, Wang K-A, Hager F T, Holden J M, Wang Y, Lee W-T, Bi X-X, Eklund P C, Cornett D S, Duncan M A and Amster I J 1993 *Science* **259** 955
- van Loosdrecht P H M, van Bentum P J M and Meijer G 1992a *Phys. Rev. Lett.* **68** 1176
- 1993a *Chem. Phys. Lett.* **205** 191
- van Loosdrecht P H M, van Bentum P J M, Verheijen M A and Meijer G 1992b *Chem. Phys. Lett.* **198** 587
- van Loosdrecht P H M, Verheijen M A, Meekees H, van Bentum P J M and Meijer G 1993b *Phys. Rev. B* **47** 7610
- Wentink T Jr 1958 *J. Chem. Phys.* **29** 188
- Zhou P, Rao A M, Wang K-A, Robertson J D, Eloi C, Meier M S, Ren S L, Bi X-X and Eklund P C 1992 *Appl. Phys. Lett.* **60** 2871