

Reaction of Molecular Oxygen with C₆₀: Spectroscopic Studies

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Using both freshly sublimed powders and evaporated thin films, the reactivity of C₆₀ towards molecular oxygen has been demonstrated using the techniques of X-ray diffraction, X-ray absorption, photoemission and infrared spectroscopy. At ambient temperature a molecular intercalation compound is formed, characterised by oxygen-rich surface and sub-surface regions. At higher temperatures oxidation to CO₂ is preceded by the formation of various carbon suboxide intermediates, as reported in the literature.

The reaction of C₆₀ with molecular oxygen is of interest for two reasons: first, the results of many other investigations on fullerene in the solid state depend on the integrity of the samples used. In particular, oxygen-induced slow modifications of sample materials may have serious implications for experimental data thought to be characteristic of the pristine material. Secondly, an understanding of the oxidative degradation of fullerenes may help us to understand more about the chemistry of this novel modification of carbon. The issue has already attracted considerable interest in the literature. Weight uptake data under various conditions¹⁻³ clearly indicate that C₆₀ is reactive towards molecular oxygen. This can also be seen from density measurements of single crystals which always yield values of ca. 1.72-1.73 g cm⁻³ compared with the theoretical density of 1.69 g cm⁻³. The reaction of C₆₀ at ambient pressure and temperature with molecular oxygen to form an epoxide has been reported in a photoemission study.⁴ A Raman band at 1469 cm⁻¹ after exposure of the pure material to oxygen supports this observation.⁵ Moreover, a recent EPR study⁶ shows that carbon-centred spins are formed after exposure of cleaned C₆₀ to oxygen at ambient temperature. The reversible formation of an oxide and the formation of another irreversible compound not susceptible to gas exchange with nitrogen were also noted. Heating to 530 K caused a further EPR-active oxide to form irreversibly in significant quantities. Emission FTIR studies⁷ have shown that controlled thermal oxidation produces vibrational bands characteristic of various carbon suboxides: 90 min at 523 K in 250 mbar oxygen is sufficient to degrade the molecule completely. We also note that a fullerene epoxide, C₆₀O, has been prepared by photo-oxidation of C₆₀ in benzene and subsequently characterised.⁸

The reactivity of fullerene towards oxygen has recently been compared to that of activated carbon,⁹ an analogy already stressed in a characterisation of molecular incorporation, or intercalation, in C₆₀¹⁰ in which EPR data were also reported. The intercalation of molecular oxygen has been further substantiated by high-pressure NMR data¹¹ and by thermal desorption experiments.¹² In this latter study the molecular nature of the intercalated oxygen was shown by isotope labelling. The interstitial, octahedral voids are thought to be the intercalation sites. All this information shows that pure solid C₆₀ is reactive towards molecular oxygen under mild conditions in the dark and that its subsequent oxidation leads not directly to CO and CO₂ but rather to several carbon suboxide intermediates. Fullerene

molecules in solution, on the other hand, seem to be stable in air when light is excluded.

The uptake of oxygen by solid C₆₀ is an interface process which is likely to be dramatically dependent in its kinetics on defect density and other diffusion-controlling structural features. Hence, the sensitivity towards oxygen will depend greatly on the crystal quality; steady-state conditions may be reached in a matter of minutes for powders and defective films, but only within days for pristine single crystals. The present paper describes the characterisation of C₆₀ after both intercalation and reaction with oxygen using various spectroscopic techniques; it focusses on the reactivity of both powders and thin films of C₆₀ towards ambient (or close to ambient) oxygen pressures at various temperatures.

Experimental

C₆₀ was prepared by the electric arc method. Graphite rods (6 mm od) were transformed with dc current in an He atmosphere (300 mbar) into fullerene black which was extracted with toluene. The raw product was purified by column chromatography (toluene-active carbon-silica gel-alumina) and checked for phase purity by UV-VIS and IR spectroscopies and analytical HPLC. The solvated solid was kept in the dark and stored no longer than one week. Oxygen-free C₆₀ was prepared from a fullerene fraction which was never exposed to air during purification in solution and subsequently triply sublimed.

X-Ray diffraction was carried out with Cu-K α radiation using STOE STADI P diffractometers. High-resolution data were collected in the focussing Debye-Scherrer transmission geometry with samples sealed in Lindemann tubes in a glove box under Ar. *In situ* heating experiments were conducted in the Bragg-Brentano geometry on a modified Bühler camera equipped with purified-gas control systems and an on-line mass spectrometer (Balzers QMG 402) for analysis of the effluent gases. In the same way pellets for FTIR transmission experiments were also prepared in a glove box and transferred to an environmental cell filled with argon.

Photoelectron spectroscopy in the core (XPS) and valence (UPS) regions as well as near-edge X-ray absorption spectroscopy (XAS) were carried out at the Berlin synchrotron radiation source BESSY on the HE-PGM II and SX-700 II monochromators. The C 1s XPS experiments were carried out at excitation energies sufficient to yield electron kinetic

energies of ca. 170 eV as measured with a Vacuum Generators CLAM electron analyser. Binding energies were determined by reference to the corresponding spectrum of highly oriented pyrolytic graphite (HOPG). The XAS data were collected in the total yield mode. Films of C_{60} were prepared on cleaned Si(100) substrates with a thickness such that the substrate signal was just no longer detectable in XPS. A Knudsen cell furnace loaded with pre-sublimed fullerene was used for deposition with the substrate at 300 K in an attached UHV preparation chamber. The latter could also be backfilled with oxygen up to 500 mbar.

Results

Powders

In order to test the possible effect of intercalated species on the structure of C_{60} a sample of chromatography-purified material stored in air for five days was subjected to an *in situ* powder X-ray diffraction heating experiment. Analysis of the sample by XPS (in a KRATOS XAM 800 instrument with Mg-K α radiation) gave a C 1s peak at 285.0 eV (FWHM 1.45 eV) as well as a broad O 1s line at 533.2 eV (FWHM 3.2 eV) and indicated a composition in the surface-sub-surface region of $C_{60}O_{10.5}$. The material was wetted by water and contained, within the sample volume analysed by XPS, a significant amount of water, as shown by the high O 1s binding energy. A low-energy shoulder on the O 1s peak at 531 eV, however, indicated that such material contains, besides residual solvents and water, molecular oxygen. This is in agreement with our earlier isotope labelling thermal desorption experiments.¹² A dry, clean nitrogen stream (2 ppm of oxygen at the outlet of the X-ray camera) was passed over the sample to allow a significant fraction of the solvents to be removed when the sample is kept at 330 K. After this cleaning the X-ray diffractogram showed only the peaks characteristic of pure C_{60} .

The sequence of X-ray diffractograms upon heating this material is summarised in Fig. 1. Up to 570 K no significant effect on the (220) and (311) reflections occurred, indicating the overall thermal stability of the crystalline material. Significant changes are observed, however, for the (111) and, less pronounced, for the (222) reflections which are known to be sensitive to stacking faults in the fcc lattice of C_{60} .¹³ The changes in intensity of the two components of the (111) reflection are presented in the inset of Fig. 1 (the positions and widths are barely affected). The top curve shows that the integrated intensity of the main component of the (111) reflection (situated at the expected position) goes through a maximum at 400 K. This maximum occurs exactly at the maximum in the oxygen desorption signal found in thermal desorption experiments.¹² If desorption alone were to occur, a step and not a maximum would be expected. The presence of a peak can be explained, however, by the slow uptake of gases from the protective environment. At temperatures above 400 K the mass spectrometer monitoring the effluent gas indicated that residual oxygen was removed from the stream. This observation illustrates the sensitivity of purified C_{60} to traces of oxygen at temperatures high enough for the activation energy barrier for transport from the surface region into the bulk of the sample to be overcome.

The splitting of the (111) reflection is induced by disorder in the solid and is not affected by the desorption process at 400 K. It disappears abruptly at 550 K as shown by the lower trace in the inset of Fig. 1, indicating that the annealing of the sample is completed. At this temperature the desorption of oxygen from a sample rich in stacking faults was also found to be complete.² Re-cooling to 300 K and repeating the experiment show that the intensity changes of the main line occur again, indicating a reversible process, but the disorder peak does not reappear. It was found that heating the sample stepwise to 600 K caused sudden disruption of the crystals with a transformation of the sample into an amorphous state,

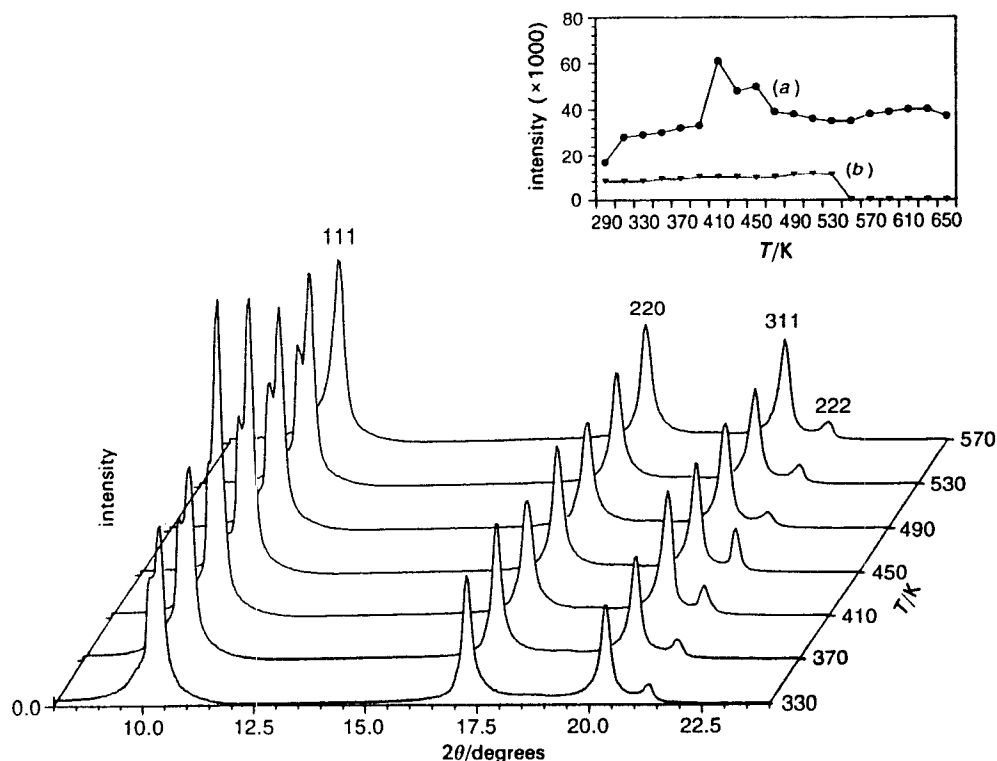


Fig. 1 X-Ray diffractograms obtained on heating C_{60} to 570 K after exposure of the clean powder sample to air for five days. Inset: The intensities of the two components of the (111) reflection; ●, main line; ▼, disorder line.

similar to that noted in the literature for C_{60} oxidation at 573 K in flowing oxygen.¹⁴

These observations suggest the participation of an intercalated species in determining the crystal properties of C_{60} . Incorporated molecules are present and show sufficient long-range order that a modulation of certain structure factors of the underlying host lattice occurs. This is further illustrated by Table 1 which shows selected diffraction intensities for C_{60} in its clean (freshly sublimed) state and after loading with oxygen or Ar at 300 K and ambient pressures. The intensity distribution for the pattern of the sublimed material is closest to the theoretical one based upon the pure C_{60} structure.¹⁵ The systematic modulation of intensities without significant changes in lattice parameters indicates the localisation of additional scattering power in the voids of the host crystal. The fact that Ar can also cause such effects shows that covalent bonding is not a prerequisite.

To illustrate further the sensitivity of polycrystalline purified C_{60} to air we show, in Fig. 2, FTIR transmission spectra of clean material and then of the same sample after exposure to air for 15 min. The clean C_{60} spectrum is in good agreement with the results of Chase *et al.* for high vacuum sublimed thin films.¹⁶ The prominent bands at 1429, 1182, 576

and 527 cm^{-1} are due to the dipole-active T_{1u} modes. The uptake of molecular water (broad line at *ca.* 1630 cm^{-1}) and of molecular oxygen (main line at 1382 cm^{-1}) is clearly visible in the spectrum after exposure to air. The IR activity of the O_2 molecules is due to symmetry reduction at the intercalation site; the site group symmetry must be C_{2v} or lower. It should be noted that C_{60} incorporates oxygen in a similar way to carbon black. The bottom spectrum in Fig. 2 illustrates that the same band at 1382 cm^{-1} is observed for a sample of commercial carbon black (FW-1, Degussa, BET surface area 236 $m^2 g^{-1}$) which was heated in vacuum to 650 K and then exposed to air.

Films

The film experiments were undertaken in order to simulate the effect of oxygen intercalation by powder samples of C_{60} . Film 1 was grown on a silicon substrate at 300 K in the presence of 5×10^{-5} mbar oxygen. Films 2, 3 and 4 were grown in vacuum at 300 K and then exposed to 500 mbar oxygen at various temperatures for 5 min.

Film 1 showed in XPS a small oxygen 1s peak corresponding to 0.5 atom% or, alternatively, a composition of $C_{60}O_{0.3}$. The effect of oxygen incorporation on the C 1s absorption edge is negligible, as shown in Fig. 3. No additional σ^* intensity (indicative of C—O bonds) and no loss of π^* intensity (indicative of a change in overall electronic structure) are detectable. The only significant difference is a small, uniform shift of the spectrum by *ca.* 100 meV to higher excitation energy. That the oxygen maintains its molecular integrity is seen in the corresponding O K-edge difference spectrum (inset, Fig. 3). Despite the poor signal to noise ratio due to the low oxygen concentration, the $1\sigma-\pi_g^*$ resonance is clearly observed at almost exactly the gas-phase value of 530.8 eV, showing that the $1\pi_g$ level is occupied to the same extent as in the free molecule. Furthermore, the structure at higher excitation energy, although affected by monochromator background structure, shows the characteristic minimum at 534 eV due to exchange splitting of the σ_u resonance.¹⁷ When this film is heated slowly to 700 K the oxygen does not react with the C_{60} but is desorbed at *ca.* 400 K, as might be expected both from the TPD² and the XRD experiments on the bulk material. Since the detection sensitivity for possible oxidation products in the XAS experiment is lower than in TPD, where a small amount of CO_2 emission from irreversible oxidation was found, we conclude that other experiments reported in the literature using similar spectroscopic techniques may not be sufficiently sensitive to monitor the effects of oxygen.

The oxygen-treatment temperatures of 300, 400 and 600 K for films 2, 3 and 4 were chosen from the TPD experiment² since they correspond to the onset and the maximum in the desorption rate as well as to the beginning of CO_2 evolution, respectively. The C 1s near-edge spectrum is sensitive to all these treatments, *i.e.* even at 300 K a distinct loss of intensity of the π^* absorption bands can be detected, as shown in Fig. 4. In particular, a distinct shift of intensity from the two π^* resonances at 284 and 287 eV to higher π^* resonances and to σ^* resonances occurs as a function of increasing temperature. Note also the general gain in intensity in the σ^* region. No new sharp features accompany these intensity changes.

In order to investigate the bonding state of the oxygen, the corresponding O 1s XAS data for films 1, 3 and 4 are compared in Fig. 5. (Unfortunately, these measurements were carried out during beamtime on the HE-PGM II monochromator at BESSY. Normalisation problems due to background structures prevented observation of the O 1s signal from film 2. For this reason the spectrum from film 1 taken

Table 1 X-Ray diffraction line intensities for freshly sublimed C_{60} as well as for C_{60} loaded with argon and oxygen

treatment	intensity (arb. units)		
	(111)	(220)	(311)
sublimed, He	110	122	100
Ar, 300 K, 1 bar	132	129	100
O ₂ , 300 K, 1 bar	138	116	100

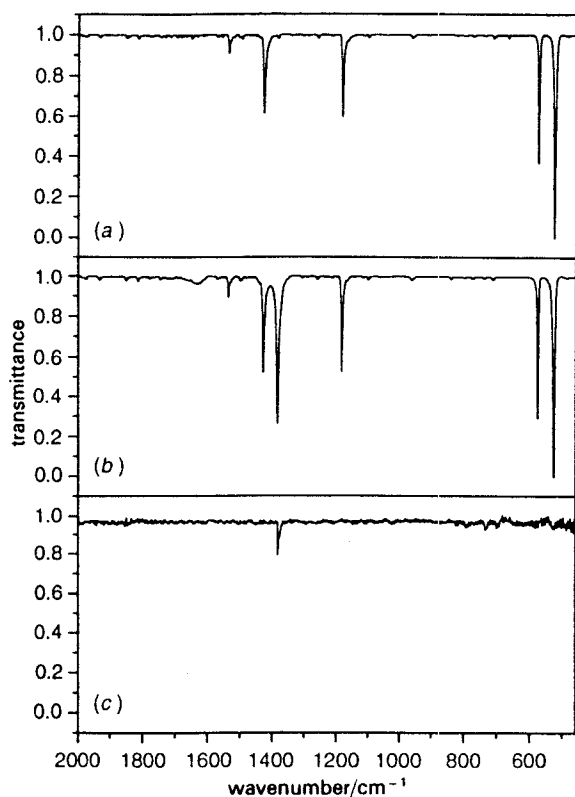


Fig. 2 FTIR transmission spectra of (a) clean C_{60} powder, (b) C_{60} powder after exposure to air for 15 min and (c) FW-1 carbon black after 15 min exposure to air

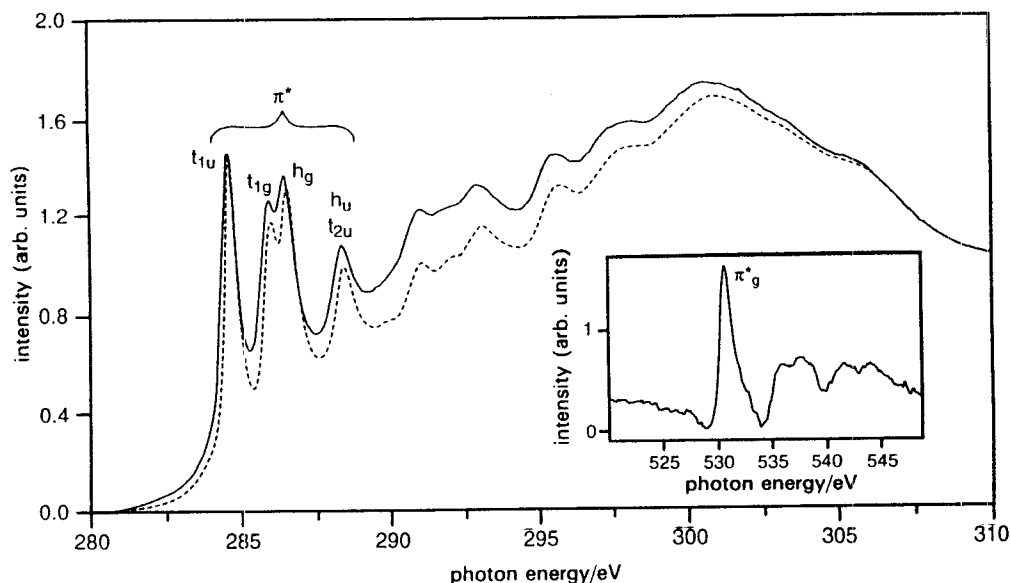


Fig. 3 C 1s XAS of a thin film of pure C_{60} (—) and of C_{60} with intercalated oxygen (---). Film 1. Inset: corresponding O 1s difference spectrum (the spectrum of pure C_{60} has been subtracted from that of C_{60} + oxygen).

on the SX-700 II monochromator is shown for comparison, *i.e.* that from the inset of Fig. 4.) Oxygen treatment at 400 K gives rise to a clear edge jump indicating a significant increase in oxygen concentration. The intensity in the π^* region is greatly diminished since the oxygen 2p orbitals forming the hitherto partially occupied $1\pi_g$ orbitals are now involved in σ -type bonding. At 600 K the oxygen concentration has further increased. The near-edge structure showing both π^* and σ^* resonances points to the presence of carbonyl-like C=O bonds.

The films were also investigated with XPS. The C 1s spectra recorded with 460 eV excitation energy are compared in Fig. 6(a). Note that the C 1s binding energy for pure C_{60} is

determined to be 284.7 eV compared with the literature value of 285.0 with Al-K α .¹⁸ This is due to a small error in the photon energy calibration. The measured linewidth (FWHM: 1.05 eV) is almost entirely determined by the monochromator resolution, since the natural linewidth is less than 650 meV.^{18,19} Up to 400 K treatment temperature very little effect is seen in the spectra except a slight broadening of the lines (FWHM: pure, 1.05 eV; 300 K, 1.10 eV; 400 K, 1.14 eV). By 600 K the spectrum has changed profoundly indicating complete oxidation of the C_{60} in the volume fraction analysed and the presence of C—O bonds (main peak at 286 eV) and C=O bonds (peak at 289.5 eV). The linewidth of 2.25 eV is probably due to charging since we are now con-

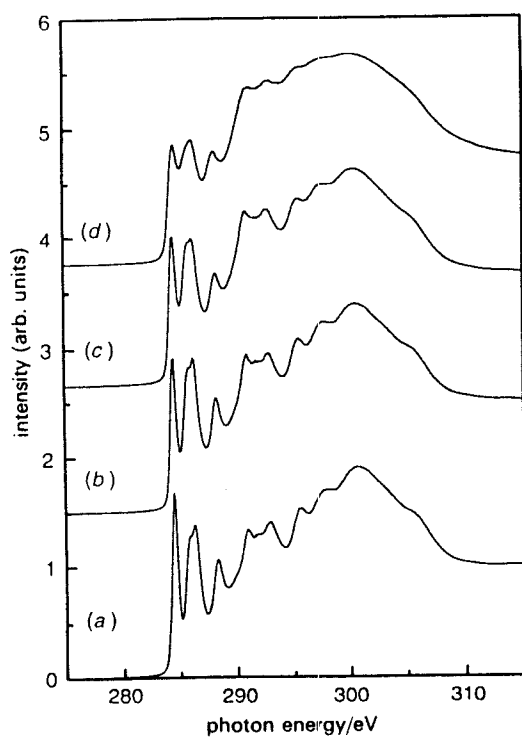


Fig. 4 C 1s XAS of thin film (a) pure C_{60} and of C_{60} after oxygen treatments at (b) 300, (c) 400 and (d) 600 K. Films 2, 3 and 4 (see text).

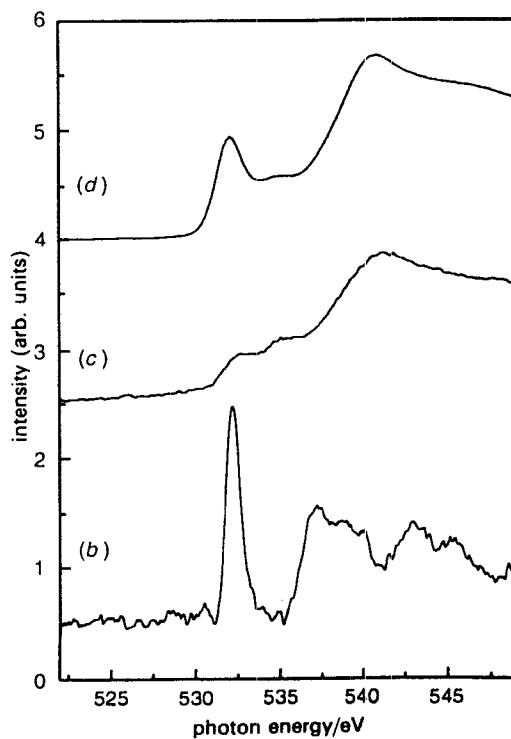


Fig. 5 O 1s XAS of thin films of C_{60} after oxygen treatments at (b) 300, (c) 400 and (d) 600 K. Films 1, 3 and 4 (see text).

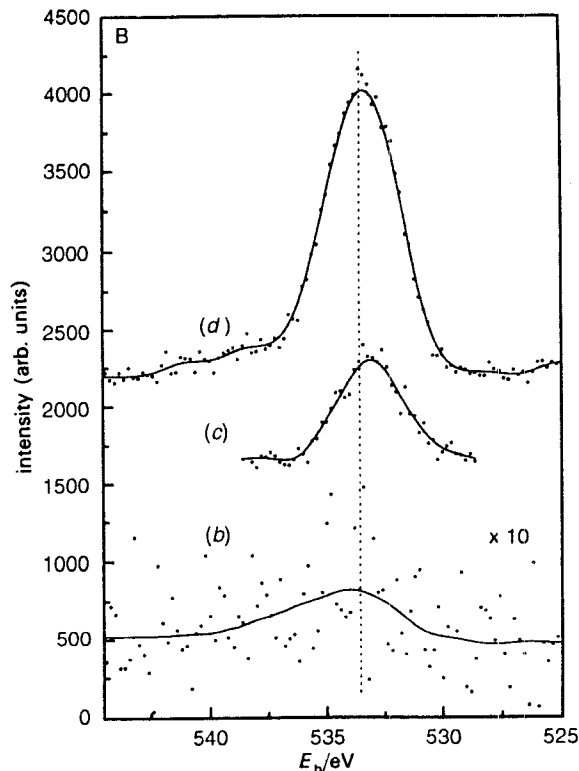
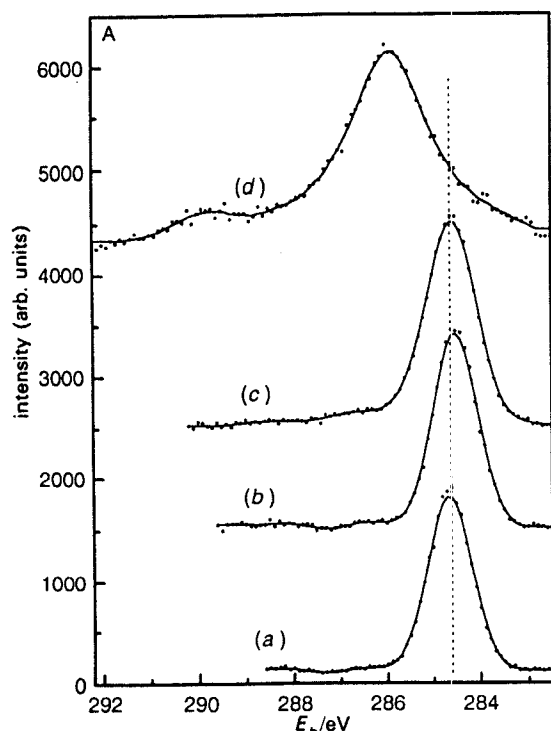


Fig. 6 A, C 1s and B, O 1s XPS of (a) a pure C₆₀ thin film and after oxygen treatment at (b) 300, (c) 400 and (d) 600 K. Films 2, 3 and 4 (see text). *hν* = 460 eV.

cerned with the heterogeneous surface of an insulator. Because of this, weaker lines arising from other, chemically inequivalent, oxidation products may not be resolved. The corresponding O 1s spectra are shown in Fig. 6(b). A small but perceptible shift in the O 1s binding energy is observed. The size of the shift is, at first sight, somewhat surprising, but a mixture of initial and final state effects may be involved. We note that chemisorbed molecular oxygen on Pt{111}, for instance, has the same binding energy as chemisorbed atomic oxygen on the same surface.²⁰

The chemical composition of the film samples derived from XPS are compared in Table 2 with the corresponding values for a powder exposed to air. It is apparent that heating solid C₆₀ in oxygen already causes severe damage to the carbon material at the temperature at which oxygen is desorbed in UHV experiments (400 K). The oxygen content, expressed as an atomic ratio, becomes erroneously high at elevated temperatures indicating that the reaction with the fullerenes must have produced smaller C₆₀O_x units which are sufficiently polar that further oxygen-containing species can be chemisorbed on their surfaces. The oxygen XPS data support this view since the average O 1s binding energy of 532.8 eV is too high to be accounted for by covalent C—O bonds (usually *ca.* 531.5 eV). A variety of lines from different molecular and atomic oxygen species are presumably superimposed to form the featureless wide band with an FWHM of 3.6 eV.

Table 2 XPS analyses of various oxygen-treated fullerene samples showing composition in the surface and near-surface region

treatment	C (atom%)	O (atom%)	composition C ₆₀ O _x
powder, 300 K air	85	15	10.5
film, evap. 1 × 10 ⁻⁵ mbar, 300 K	99.5	0.5	0.3
film, 300 K, 500 mbar	86	14	9.8
film, 400 K, 500 mbar	53	47	54.5
film, 600 K, 500 mbar	39	61	93.8

A chemical interaction between oxygen and the C₆₀ films after heating to 400 K is also indicated by the UPS data at 100 eV excitation energy shown in Fig. 7. The spectrum from film 2 at 300 K is identical to that of pure C₆₀ (not shown). At 400 K, where the carbon 1s line was still unchanged [see Fig. 6(a)] the presence of oxygen is apparent from the loss in intensity of the π-like h_u, h_g and g_g intensity and by the broad

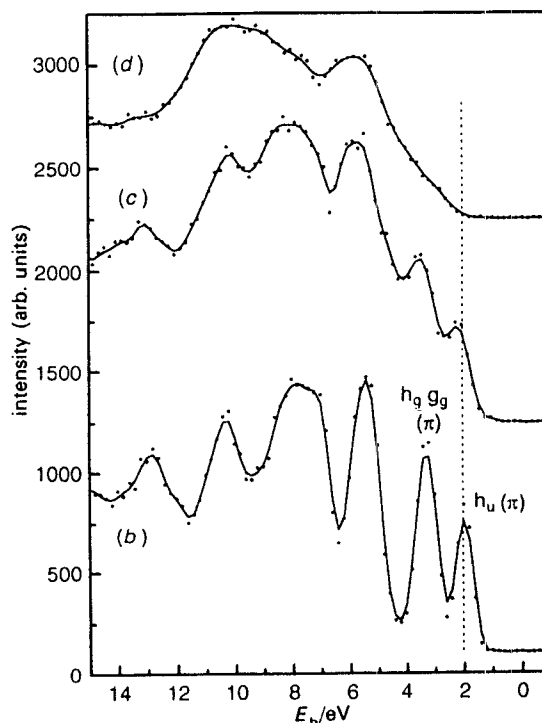


Fig. 7 UV photoemission spectra of thin films of C₆₀ after oxygen treatments at (b) 300, (c) 400 and (d) 600 K. Films 2, 3 and 4 (see text). *hν* = 100 eV.

underlying peak above ca. 3 eV binding energy arising from the O 2p-derived states. At 600 K the molecular fingerprint of the C₆₀ molecule has disappeared as oxidation in the near-surface region is completed. This spectrum is similar to that obtained after photooxidation of thin C₆₀ films.²¹ The radical loss of the fullerene features in UPS is not in contradiction to the more gradual change in XAS (see Fig. 4) since the information depths of the two techniques are different. Even at 100 eV excitation energy UPS is significantly more surface sensitive than the total-yield XAS experiment for which there is a large contribution of secondary electrons from the bulk.

Discussion

The present experiments demonstrate the reactivity of purified C₆₀ towards oxygen and show how the nature of the interaction depends on sample temperature. Low partial pressures of oxygen (2 ppm in nitrogen or 2×10^{-6} mbar total pressure in the XRD and IR experiments on powders and 1×10^{-5} mbar in the UHV growth experiment) are sufficient to produce oxygen intercalation. The XRD and XAS experiments clearly reveal the bulk sensitivity of C₆₀ to oxygenation and indicate that photoelectron spectroscopy also gives a qualitative picture of what happens in the bulk despite its surface-sensitive nature. It is to be expected that a concentration gradient of oxygen exists within the crystal reducing the average concentration of oxygen to significantly below that implied by the composition C₆₀O_{9,8} measured for film 2 at 300 K. An average composition of C₆₀O₂ would be consistent with the anomalously high density of polycrystalline C₆₀ (ca. 1.73 g cm⁻³) observed for single crystals and correspond to a weight increase of 1.8%. So far, we have been unable to detect the latter in gravimetric experiments owing to the large errors involved when handling small amounts of well purified material under rigorous exclusion of oxygen.

The present findings support our earlier TPD results¹² and clearly indicate that purified crystalline C₆₀ is not stable with respect to oxygen uptake. The interaction leads to a variety of products ranging from molecular intercalation compounds to CO₂. Complete oxidation is apparently preceded by the formation of various carbon suboxides, including peroxide and epoxide species. Several of these states have been described before in the literature (see Introduction) but not as a sequence of one and the same reaction. A schematic diagram representing the reaction of C₆₀ with oxygen is shown in Fig. 8. We note that the free molecule does not react with oxygen in the dark under ambient conditions. The kinetics of the uptake by the solid are controlled by the properties of the gas/solid interface and hence by the quality of the surface. Well shaped smooth, single-crystal surfaces will react more slowly than powders or thin films. Indeed, large (few mm) shiny single crystals are known to be relatively stable in oxygen. The low-temperature reaction is not fully reversible leaving behind, even after degassing in UHV, a small amount of chemically reacted, and probably polymeric, C₆₀ fragments. They are probably located at the surfaces of individual crystallites in powder material and may influence the transport properties of superconducting intercalation compounds. It is known that these surface regions cannot be intercalated and represent conduction barriers within the solid material.

We conclude with the following recommendations for handling C₆₀ materials in order to ensure that the properties of the sample are actually those of authentic fullerene material:

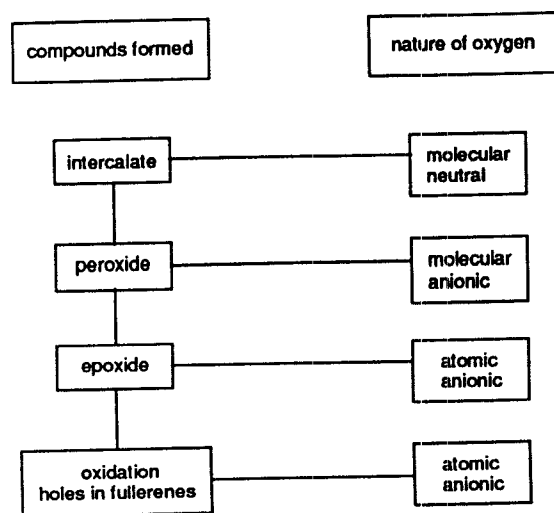


Fig. 8 Schematic of the interaction of oxygen with solid C₆₀

(1) Exposure to air or oxygen must always be avoided. Even sublimed C₆₀ is irreversibly modified after contact with oxygen or air under any conditions.

(2) Degassing can greatly reduce the abundance of oxygen after heating 570 K. At this temperature the sample is, however, extremely sensitive to traces of oxygen as present in purified inert gases or in high vacuum.

(3) Dissolved or solvent-saturated forms of fullerene in the absence of light are the most stable forms for storage. The material should be solidified and sublimed immediately prior to use.

Finally, we note that freshly sublimed C₆₀ could be an efficient ultra-purification agent for inert gases and glassware. As noted above, however, its efficiency drops with the surface perfection of the crystallites.

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