

## Interaction of Nitrogen and Oxygen with C<sub>60</sub>

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Evidence is presented for the strong interaction of nitrogen and oxygen with buckminsterfullerene.

The chemistry of buckminsterfullerene, C<sub>60</sub>, has attracted world-wide attention in the last few months. C<sub>60</sub> exhibits many novel properties. It undergoes facile one-electron reduction to give various anionic species<sup>1,2</sup> and can produce singlet oxygen with high quantum yields.<sup>3</sup> It is reported that C<sub>60</sub> is oxidised by solid O<sub>2</sub> on exposure to low- or high-energy photons.<sup>4</sup> Interaction of C<sub>60</sub> with N<sub>2</sub> has not been studied hitherto

although one would expect interesting adsorbed species to be formed on the surface, considering that strongly-bound molecular species with a bond order between 1 and 2 have been found on a carbided nickel surface.<sup>5,6</sup> We have studied the interaction of N<sub>2</sub> with multilayer C<sub>60</sub> films by employing X-ray photoelectron spectroscopy and for comparison purposes, have also examined the interaction of O<sub>2</sub> with C<sub>60</sub> films.

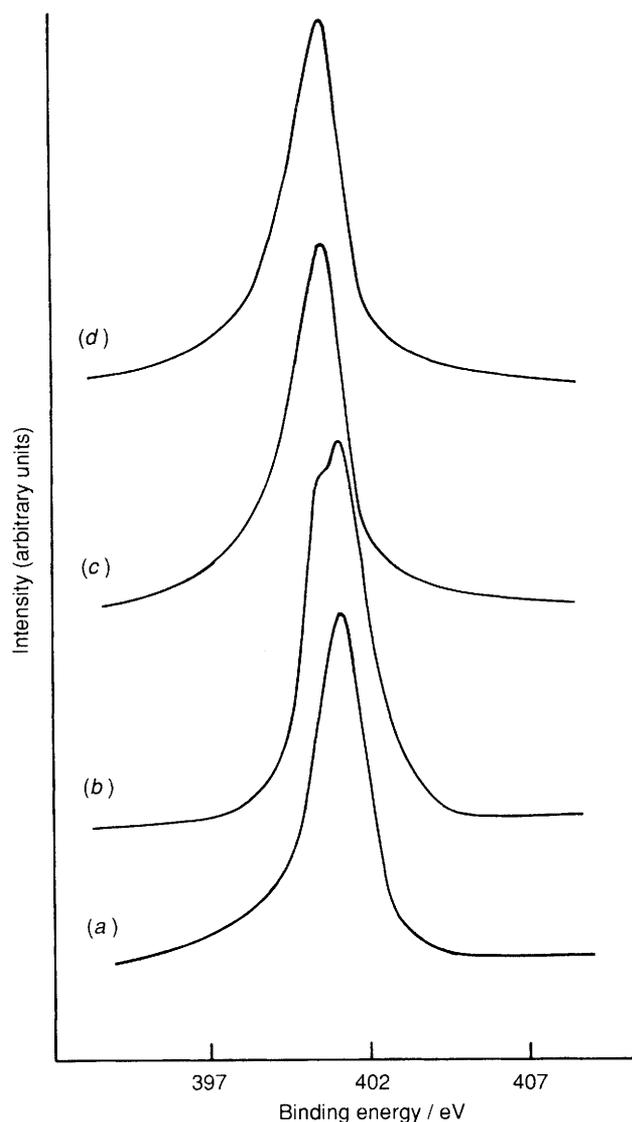


Fig. 1 N(1s) X-ray photoelectron spectra of  $N_2$  adsorbed on  $C_{60}$ : (a) at 80 K; (b) on warming to 300 K; (c) on further warming to 450 K; and (d) on recooling to 300 K

In addition preliminary experiments were carried out to see if nitrogenous derivatives of  $C_{60}$  are formed if vaporization of graphite is carried out in a partial atmosphere of  $N_2$ .

$C_{60}$ , prepared by the contact-arc vaporization of graphite in a He atmosphere by employing a locally fabricated generator,<sup>7</sup> was purified by chromatography<sup>8</sup> and the identity ascertained by mass spectrometry, UV-VIS and  $^{13}C$  NMR spectroscopy. Layers of  $C_{60}$  were deposited on a polycrystalline Au foil. Photoelectron spectra were recorded with a VG ESCA 3 MkII spectrometer fitted with a sample preparation chamber, by employing Al-K $\alpha$  (1486.6 eV) or He-II (40.8 eV) radiation under an operating vacuum of  $\approx 4 \times 10^{-10}$  Torr. The O(1s) and N(1s) binding energies were referenced with respect to the Au(4f) binding energy (84.0 eV). The  $C_{60}$  films were exposed to  $N_2$  and  $O_2$  under different conditions in the sample preparation chamber.

In Fig. 1 is shown the N(1s) spectrum of  $N_2$  adsorbed on a multilayer film of  $C_{60}$  at 80 K. A single sharp feature around 400.6 eV is observed, unlike  $N_2$  adsorbed on most transition-metal surfaces (in the  $\gamma$ -state<sup>6</sup>) wherein two relative broad features at ca. 401 and 405 eV are generally found due to the

screened and the unscreened final states, respectively.<sup>6</sup> A single N(1s) feature in the 399–400 eV range is found on transition-metal surfaces when  $N_2$  is strongly chemisorbed in the  $\alpha$ -state<sup>6</sup> with an N–N bond order between 1 and 2. We believe that the N(1s) peak at ca. 400.6 eV found at 80 K on the  $C_{60}$  films is due to a strongly chemisorbed molecular species, **I**, the sharpness of the feature being suggestive of the presence of a well-defined single species (note that graphite does not interact with  $N_2$  either at 80 or 300 K). The absence of a feature due to the unscreened state also suggests that the  $N_2$  species is strongly bound to the surface. This  $N_2$  species does not desorb even at 300 K, unlike the weakly chemisorbed  $\gamma$ -species on transition-metal surfaces which desorbs well below 300 K. The N(1s) spectrum at 300 K (Fig. 1) also shows the emergence of a new sharp feature at a lower binding energy (400.2 eV). This would represent another chemisorbed state, **II**, of  $N_2$  on  $C_{60}$ . On warming to 450 K, we only see the 400.2 eV feature indicating that species **I** is completely transformed into **II**. We consider the occurrence of such chemisorbed states of  $N_2$  on  $C_{60}$  to be most interesting. It is possible that the structure of this species is one where a weakened N–N bond (ca. 1.3–1.4 Å) lies side-on to a C–C bond of  $C_{60}$ . We have not found any evidence for the formation of dissociated nitrogen species on  $C_{60}$  up to 450 K.

Unlike in the case of  $N_2$ ,  $C_{60}$  films exposed to oxygen or air (without any special irradiation) show evidence for reactive interaction, with an O(1s) feature being observed at ca. 532.5 eV at 300 K due to oxygenated  $C_{60}$ , probably involving an epoxide-like linkage as in graphitic oxide, rather than a carbonyl function. Accordingly, the 532.5 eV feature remains on the surface even at 450 K. Graphite itself does not interact with oxygen at 300 K and oxidation of graphite occurs only on interaction with atomic oxygen or oxygen plasma.<sup>9</sup> It is likely that the oxidation of  $C_{60}$  probably occurs through the  $O_2^-$  species<sup>10</sup> [O(1s), 534.2 eV] initially formed on the surface upon adsorption of  $O_2$  at low temperatures; the  $O_2^-$  species disappears below 200 K from the surfaces of clean as well as oxygenated  $C_{60}$ .

The above results encouraged us to carry out contact arc-vaporization of graphite in a partial atmosphere of  $N_2$ , by leaking in  $N_2$  gas at the same rate as helium. The toluene extract of the soot, after removal of the solvent, showed the presence of nitrogenous derivatives of  $C_{60}$  as evidenced from chemical analysis and mass spectrometry. Interestingly, these derivatives seem to involve addition of nitrogen to  $C_{60}$  together with some substitution of carbon by nitrogen. Further studies of the interaction of nitrogen with  $C_{60}$  are in progress.

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