

Buckminsterfullerene, C₆₀: Improved synthesis, electron microscopy, electron states, anions and related aspects

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Abstract. Buckminsterfullerene, obtained in good yields at high rates by a suitably designed generator, has been characterized by electron microscopy and in terms of an approximate energy level diagram; C₆₀ undergoes four reversible one-electron reductions giving rise to anionic species and interacts with tetrathiafulvalene to form a charge-transfer complex in the ground state.

Keywords. Buckminsterfullerene, C₆₀; approximate energy level diagram; reversible one-electron reductions; closed-cage molecules.

1. Introduction

The closed-cage molecules of carbon, the fullerenes, and in particular buckminsterfullerene, C₆₀, first discovered by Kroto *et al* (1985) have become a topic of intense research after the synthetic procedure to prepare macroscopic quantities became available (Kratschmer *et al* 1990). In our efforts to investigate the structure, properties and reactivity of C₆₀, we have designed a generator which produces C₆₀ in high yields at a fast rate. In this communication, we describe the synthesis and characterization of C₆₀, by means of electron microscopy, electron states, cyclic voltammetry and other techniques. We have given a satisfactory energy level scheme consistent with the electronic absorption spectrum and the UV photoelectron spectrum. We report four one-electron reversible reduction potentials of C₆₀ giving rise to the different anions, besides reliable electronic absorption spectra of the mono and di-anions. We have also examined the interaction of C₆₀ with various electron donor and acceptor molecules.

We have prepared C₆₀ by contact-arc vapourization of graphite in a helium atmosphere. The C₆₀ generator fabricated by us has a water-cooled copper vessel fitted with two water-cooled copper electrode holders housed in a stainless vacuum steel vessel mounted on a diffusion pump through a cold trap (liquid N₂). The graphite electrodes are held at loose contact, with their tips sharpened to a conical shape. One of the electrodes can be readily moved horizontally from outside in order to facilitate

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the maintenance of the arc over extended periods. By employing a current of 150 amps or less, we have obtained C_{60} from the soot after separation and purification, the purity having been checked from mass spectrometry and ^{13}C NMR spectroscopy (Haufler *et al* 1990; Taylor *et al* 1990; Cox *et al* 1991). The yield of C_{60} with respect to the soot was 30%. Furthermore, by manipulating one of the electrodes from outside we could obtain C_{60} at high rates (50 mg in ~ 30 min). We believe that this innovation is worthy of notice.

Scanning electron micrographs of the C_{60} particles obtained after removal of the solvent show spherical aggregates of 1–5 microns (figure 1a). High-resolution electron micrographs not only show lattice fringes corresponding to $c/2$ ($\sim 8 \text{ \AA}$) as in figure 1b, but also the closed-packed arrangement of C_{60} molecules with a diameter of $\sim 7 \text{ \AA}$. In the inset of figure 1b we show an image where the nearly circular white

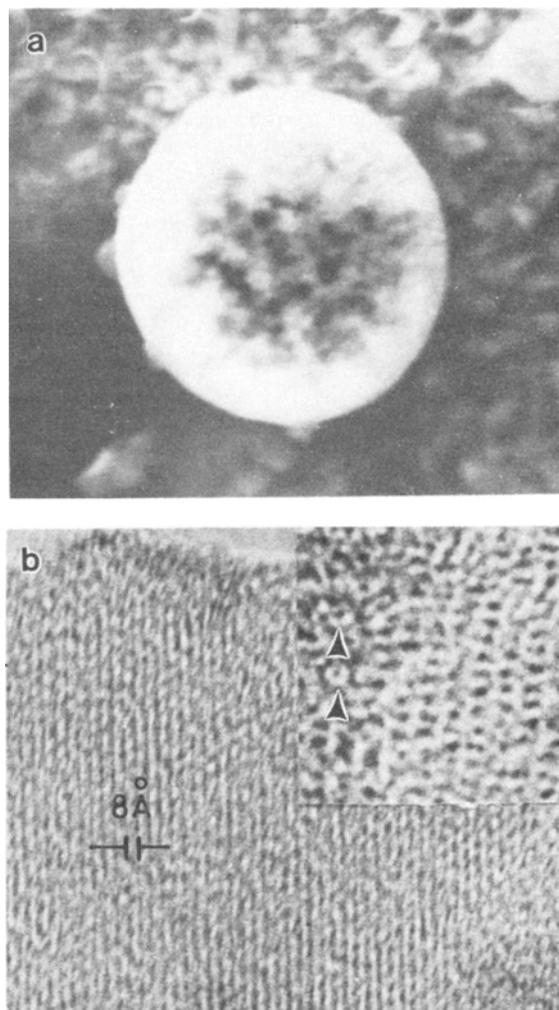


Figure 1. (a) Scanning electron micrograph showing spherical aggregates of C_{60} . (b) Lattice fringes in the transmission electron micrograph; inset shows close-packed C_{60} molecules.

features with central black spots represent the projection of the hollow cage of the C_{60} molecule.

The electronic absorption spectrum of C_{60} in *n*-hexane solution recorded by us shows distinct maxima at 213, 257 and 328 nm ($\log \epsilon$, 5.1, 5.2 and 4.7 respectively) and a broad band centred around 555 nm; there is also a sharp feature at 404 nm in agreement with Hare *et al* (1991b). We are able to understand the spectrum by taking the first three π orbital energies to be approximately equal to the ionization energies from the UV photoelectron spectrum (Lichtenberger *et al* 1991). The ionization energies are at 7.6 (h_u), 8.9 ($g_g + h_g$) and 10.8 eV ($g_u + t_{2u}$). In figure 2 we show the energy level diagram of C_{60} which also indicates the various π - π^* transitions; in this diagram we have made use of the fact that the differences in some of the transition energies are close to the differences in the π orbital energies. The longest wavelength π - π^* transition around 550 nm corresponds to HOMO-LUMO separation of 2.2 eV, in agreement with theoretical expectations (Fowler and Woolrich 1986; Bakowies and Thiel 1991) and the electron energy loss spectrum (Hansen *et al* 1991). The sharp 404 nm feature is likely to be due to the π_2 - π_1^* (rather than the π_1 - π_2^*) transition as shown in figure 2. Some of the structure in the 550 nm band seems to correspond to the known vibrational frequencies of the molecule (Hare *et al* 1991a). The UV absorption bands of C_{60} show solvent red-shifts in polar solvents (Rao *et al* 1976) indicating an increase in the dipole moment on excitation. The red-shifts of the 328 nm band in CH_3CN and DMSO solvent are 92 and 278 cm^{-1} respectively with respect to *n*-hexane.

Cyclic voltammetry of C_{60} in CH_2Cl_2 solution carried out by Haufler *et al* (1990) with a glassy carbon electrode showed two reversible anionic forms. Dubois *et al* (1991) have more recently found four reductions in the -0.4 to -1.7 V range at a high scan rate of 20 V/s, of which only the first two at -0.44 and -0.82 V were reversible. We have carried out cyclic voltammetry as well as differential pulse

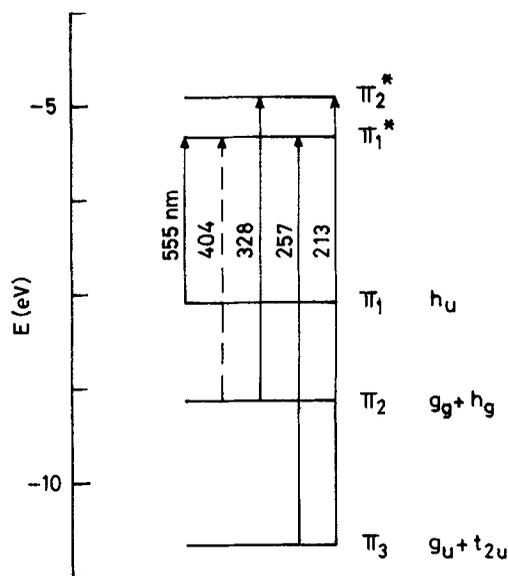


Figure 2. Approximate energy level scheme of C_{60} .

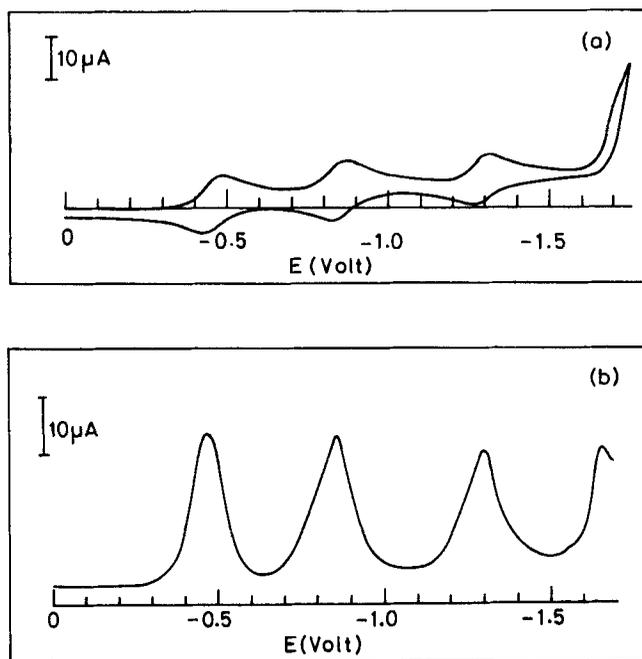


Figure 3. (a) Cyclic voltammogram of C₆₀ in CH₂Cl₂ solution (~ 1 mM, Au electrode with 0.05 M NH₄PF₆ as supporting electrolyte, scan rate 300 mV/s). (b) Differential pulse voltammogram of C₆₀.

voltammetry in CH₂Cl₂ solution with Pt, glassy carbon and Au electrodes and found four one-electron reduction peaks in the range -0.4 to -1.9 V (figure 3). The reduction potentials are -0.464, -0.856, -1.292 and -1.661 V (vs Ag/AgCl), of which the first three were fully reversible while the fourth was quasi-reversible at a slow scan of 100–500 mV/s. The four successive reduction potentials were independent of the electrode and indicate the formation of C₆₀⁻, C₆₀²⁻, C₆₀³⁻ and C₆₀⁴⁻. We could however not obtain oxidation of C₆₀ up to ~2 V.

Thin-layer spectroelectrochemical measurements carried out with an optically transparent good mini-grid electrode have enabled us to obtain good electronic absorption spectra of C₆₀⁻ and C₆₀²⁻. We show the spectra in figure 4. The UV absorption bands of C₆₀⁻, besides showing red-shifts with respect to C₆₀, are less intense as expected (Rao *et al* 1970). We also see a characteristic band at 830 nm due to C₆₀⁻ which disappears in the dianion. Our measurements also show that the two anions could be reversibly oxidized back to C₆₀.

We have investigated the interaction of C₆₀ with a variety of electron donor and acceptor molecules in hexane or CH₂Cl₂ solutions. We have found no evidence for the interaction of C₆₀ with electron acceptors such as iodine, 1,3,5-trinitrobenzene and tetracyanoethylene; this is not unexpected on the basis of the high electron affinity (Yang *et al* 1987) of C₆₀. Surprisingly, C₆₀ does not seem to interact with aromatic donors such as perylene or N,N-tetramethyl phenylenediamine. We however find evidence for the interaction of C₆₀ with tetrathiafulvalene which is a strong electron donor molecule. We have observed a charge-transfer band around 247 nm due to the

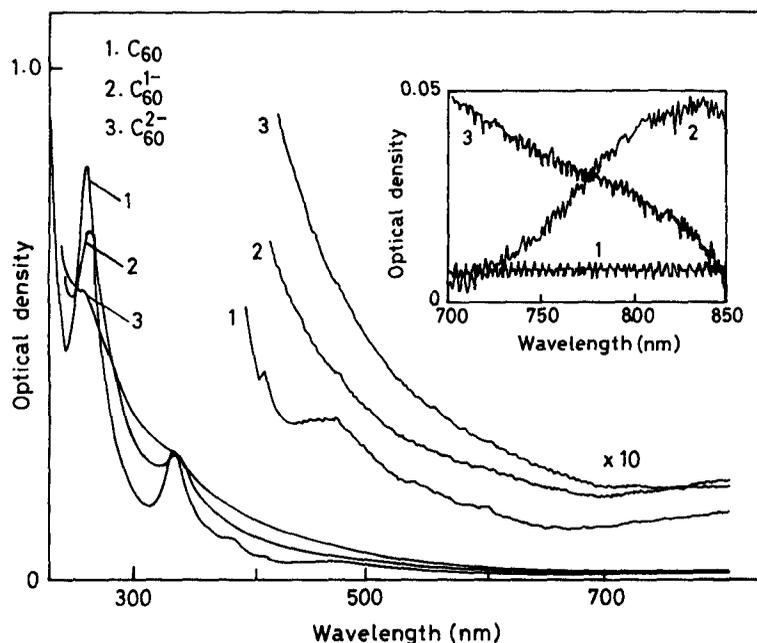


Figure 4. Electronic absorption spectra of C_{60} , C_{60}^{1-} and C_{60}^{2-} obtained using a thin-layer spectroelectrochemical cell (electrolysis time 300 s). Inset shows the spectrum in the 700–850 nm region.

C_{60} + TTF complex. We have found no evidence for the formation of exciplexes with N,N-dimethylaniline or 1,4-dicyanobenzene.

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