The fullerenes: powerful carbon-based electron acceptors

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The gaseous, solution and solid state experimental evidence for electron addition to the fullerenes is reviewed and it is shown that this class of molecules function as powerful electron acceptors. The topological character of C_{60} as described by Hückel molecular orbital theory suggests that the molecule will undergo facile reduction, but comparisons with planar conjugated hydrocarbons show that this feature alone cannot account for the very low half-wave reduction potential of C_{60}. Because of the curvature of the surface, fullerene hybridization falls between graphite (sp^2) and diamond (sp^3) and these new carbon allotropes are therefore of *intermediate*, and perhaps *variable* hybridization. According to POAV1 theory the carbon atoms in C_{60} are of $sp^{2.28}$ hybridization. It is concluded that rehybridization plays an important role in determining the electronic structure of the fullerenes and it is the combination of topology and rehybridization that together account for the extraordinary ability of C_{60} to accept electrons.

1. Introduction

The ability of the fullerenes to function as electron acceptors has been recognized since the first investigation of their chemistry (Haufler *et al.* 1990). Even before the isolation of bulk quantities of C_{60} (Krätschmer *et al.* 1990), a large electron affinity was demonstrated for this molecule in gas phase experiments (Curl & Smalley 1988).

This trend has continued with the development of the physics, chemistry and materials science of the fullerenes. In this paper some of the experiments that have thrown light on the ability of the fullerenes to accept electrons are summarized and qualitative explanations for their extraordinary electron affinity are discussed.

2. Gas phase reduction

New measurements in the gas phase have confirmed the original findings (Curl & Smalley 1988) on the electron affinity of C_{60}. The most recent experiments give an electron affinity (EA) of 2.65 ± 0.05 eV for C_{60} (Wang *et al.* 1991). Furthermore it has been shown that C_{60} and C_{70} are among the very few molecules which can bind two electrons in the gas phase (Limbach *et al.* 1991).

3. Solution reduction

The solution electrochemistry is now well developed (Haufler *et al.* 1990; Allemand *et al.* 1991; Cox *et al.* 1991; Dubois *et al.* 1991; Miller *et al.* 1992; Wudl 1992) and the most recent experiments have shown the presence of six reversible reduction waves (Xie *et al.* 1992). There is a spread in the published half-wave reduction potentials as
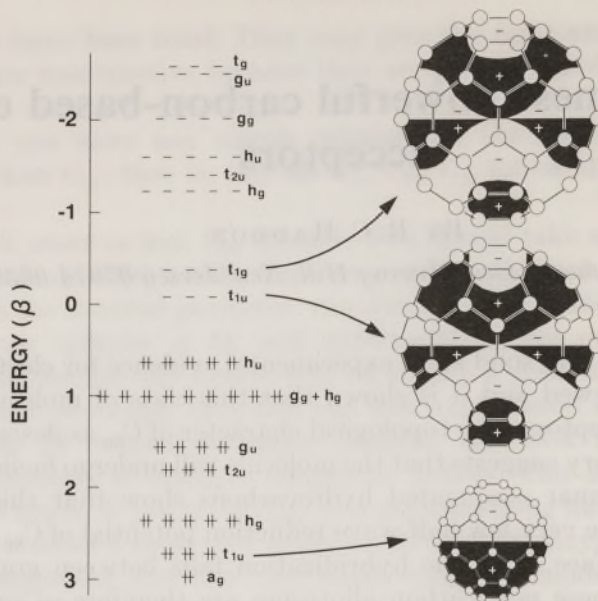
Figure 1. Hückel molecular orbital (HMO) energy levels of C_{60} together with one component of the triply degenerate t_{1u} and t_{1g} sets of molecular orbitals.

a result of the different solvents and reference systems that have been used. Of the measurements which are referenced to the standard calomel electrode, a representative first reduction potential for C_{60} is $E_{\frac{1}{2}} = -0.4V$ (SCE). There is also C^{13} NMR evidence for a highly reduced C_{60} species in THF solution in the presence of lithium metal which probably also corresponds to C_{60}^{6-} (Bausch et al. 1991). In the HMO diagram for C_{60} this reduction level corresponds to the complete filling of the t_{1u} level (figure 1). Other experiments, using lithium intercalation into C_{60}, have found evidence for even more highly reduced species, which would implicate the next set of triply degenerate levels in the HMO diagram (t_{1g}) (Chabre et al. 1992).

4. Solid state reduction

In the solid state, intercalation of C_{60} films, powders and crystals with alkali (A) metal dopants have led to new phases which may be insulators, conductors and superconductors depending on the filling of the t_{1u} level and the size of the dopant (Haddon et al. 1991; Hebard et al. 1991; Rosseinsky et al. 1991; Holczer et al. 1991; Tanigaki et al. 1991; Kochanski et al. 1992; Xiang et al. 1992; Fischer et al. 1992; Haddon 1992; Weaver 1992). For example, in the case of the A = K, Rb the A_3C_{60} phases are superconductors and the A_6C_{60} compounds are insulators. Thus when the t_{1u} level is half-filled (C_{60}^{3-}) the compounds are three-dimensional metals, but become insulators again when this level is full (C_{60}^{6-}). Recently it has been shown that the small alkali metals are able to produce A_xC_{60} phases with $x > 6$ (Fischer 1992).

Solid C_{60} also undergoes doping with alkaline earth (Ae) metals (Chen et al. 1992; Wertheim et al. 1992; Haddon et al. 1992) and Ca_5C_{60} has been shown to be a superconductor (Kortan et al. 1992). The nature of the doping with the alkaline earths is less clear than for the alkali metals. The alkali metal compounds appear to be fully charge transferred at least up to A_6C_{60} and exist as discrete phases. The alkaline earths, however, form solid solutions and the degree of charge transfer is less
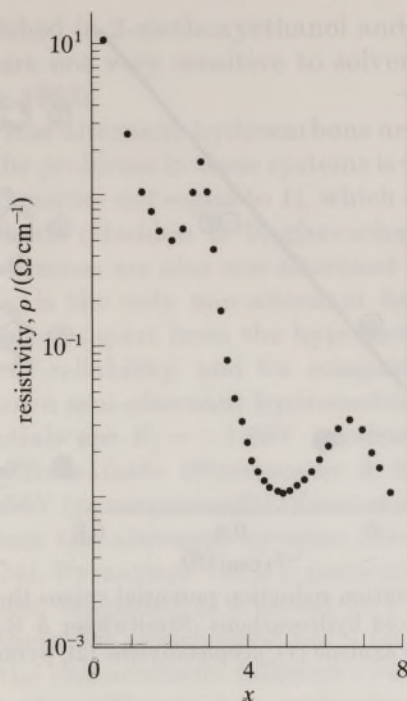
Figure 2. The resistivity of a 190 Å thick annealed Sr_xC_{60} film at 60° in UHV as a function of x (Haddon *et al.* 1992).

certain. Nevertheless, up to Ae_3C_{60}, photoemission (Chen *et al.* 1992; Wertheim *et al.* 1992), theoretical (Saito & Oshiyama 1992), and transport studies (Haddon *et al.* 1992) indicate a high degree of electron transfer and these phases correspond fairly well to C_{60}^{6-}. Beyond this level further doping apparently populates the t_{1g} level but the degree of charge transfer is uncertain for compositions in this range. For Ae_xC_{60} compositions with $x > 3$, photoemission studies suggest hybridization between the valence s-levels of the alkaline earths and the t_{1g} levels of C_{60}.

A plot of resistivity as a function of composition for a Sr_xC_{60} thin film (Haddon *et al.* 1992) is shown in figure 2 (similar behaviour is seen with Ca_xC_{60} films). There is a resistivity maximum close to the film composition Sr_3C_{60} and minima at Sr_2C_{60} and Sr_5C_{60}. The absence of a maximum at Sr_6C_{60} suggests that this composition is not fully charge transferred, and that hybridization with Sr states is now important in determining the electronic structure of the conducting phase. The nature of the doping beyond this point is even more uncertain, but the weak resistivity maximum at $x \approx 7$ in the Sr_xC_{60} thin film suggests that the t_{1g} band is effectively full at this point.

5. Theoretical interpretation within HMO theory

The basic structural features of the fullerenes have been recognized for some time. To close a sheet of carbon atoms into a fullerene, apart from six-membered rings (6MRs), spheroid formation requires the presence of 12 5MRs (Kroto *et al.* 1985; Zhang *et al.* 1986). The topological aspects of the fullerenes – placement of the 5MRs on the surface of the spheroid – is qualitatively accounted for in the simple HMO approach as shown in figure 1 for C_{60} (Haddon *et al.* 1986a). It may be seen that the two lowest unoccupied sets of molecular orbitals of C_{60} (t_{1u} and t_{1g}), bear a striking resemblance with respect to their nodal structure. To some extent this is exaggerated
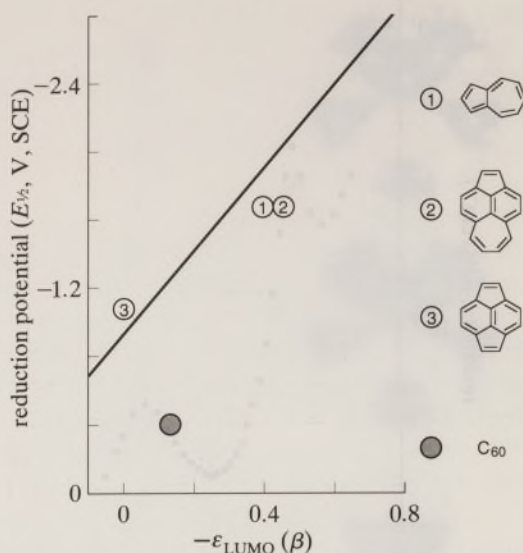
Figure 3. Regression line of the solution reduction potential versus the HMO–LUMO energy (ϵ_{LUMO}, β negative) for a series of benzenoid hydrocarbons (Streitwieser & Schwager 1962; Streitwieser 1962). The half-wave potentials for azulene (1), acepleiadylene (2), pyracyclene (3), and C_{60} are also shown (see text).

in figure 1 as there is an extra nodal plane in the t_{1g} orbitals with respect to the t_{1u} set that passes through both the apical and equatorial pairs of carbon atoms which is not visible in the orientation shown.

The other aspect of fullerene electronic structure which relates to their ability to accept electron density is the rehybridization of the carbon π atomic orbitals as a result of the curvature which is imposed on the conjugated carbon atoms by the shape of the molecules (Haddon *et al.* 1986a, b). The discussion of rehybridization effects is deferred to §6, and we begin with a treatment of the topological contribution to fullerene electronegativity within simple HMO theory. The presence of 12 conjugated 5MR in the fullerenes suggests that they will be biased towards reduction in their redox chemistry.

Although HMO theory might seem unlikely to provide a basis for the ability of conjugated organic molecules to accept electrons, it has been shown to provide a useful semi-quantitative account of the redox chemistry of benzenoid hydrocarbons and has even been used to rationalize electron affinities (Streitwieser 1962). The method is usually used to correlate the position of the first reduction wave with the eigenvalue of the lowest unoccupied molecular orbital (LUMO) of the neutral molecule. The straight line from a regression plot (Streitwieser & Schwager 1962) of the solution reduction potential versus the HMO–LUMO energy (ϵ_{LUMO}, β negative) for a series of benzenoid hydrocarbons is shown in figure 3. Although the individual points are not shown, a good linear correlation was established as expressed by the equation

$$E_{\frac{1}{2}} = (2.407 \pm 0.182)\,\epsilon_{\text{LUMO}} - 0.946 \pm 0.093, \tag{1}$$

where $E_{\frac{1}{2}}$ is the half-wave reduction potential. The experiments were carried out in dimethylformamide and the potentials measured with reference to an internal mercury pool anode; equation (1) has been corrected to the SCE reference by subtracting 0.55 V from the constant term (Streitwieser & Schwager 1962). Similar

correlations were established in 2-methoxyethanol and aqueous dioxane and it was shown that the results are not very sensitive to solvent effects (Streitwieser 1962; Streitwieser & Schwager 1962).

It is well known that non-alternant hydrocarbons are more difficult to treat with HMO theory, and one of the problems in these systems is the presence of finite π charge densities (HMO electron densities not equal to 1), which are usually overestimated by single determinant methods (Haddon & Raghavachari 1983). As a result of the presence of 5MRs the fullerenes are also non-alternant 'hydrocarbons', but because of its high symmetry C_{60} is the only non-alternant hydrocarbon with zero charge density at each carbon atom (apart from the hypothetical fullerene C_{20}).

To provide an index of reliability, and for comparison with the fullerenes, the results for three well known non-alternant hydrocarbons have been added to figure 3. The half-wave potentials are $E_{\frac{1}{2}} = -1.65$V (azulene (1)) and -1.65V (acepleiadeylene(2)) in dimethylformamide (Streitwieser & Schwager 1962; Andersen & Masada 1974) and -1.056V (pyracyclene(3)) (Trost *et al.* 1971) all versus SCE. They exhibit higher errors than the alternant systems (Streitwieser & Schwager 1962; Andersen & Masada 1974). Pyracylene (3) is a particularly appropriate comparison as this compound has been suggested as a model for C_{60} chemistry (Allemand *et al.* 1991; Wudl 1992). Furthermore pyracyclene has a non-bonding LUMO ($\epsilon_{LUMO} = 0$), which is fairly close to the characteristic fullerene LUMO on the HMO scale ($\epsilon_{LUMO} = -0.139\beta$ (C_{60}), 0 (C_{70})). According to (1), molecules with a non-bonding LUMO should be reduced at -0.946V. This is in reasonable agreement with the observed values for pyracylene with $E_{\frac{1}{2}} = -1.056$V and triphenylmethyl with $E_{\frac{1}{2}} = -0.97$V (acetonitrile, SCE reference) (Breslow & Grant 1977).

The first reduction wave for C_{60} has also been added to figure 3 and it may be seen that the ease of reduction is grossly underestimated by this correlation to the extent of about 0.85V. Thus while the topological treatment, within HMO theory, correctly suggests that C_{60} will be a strong electron acceptor, an additional factor must be considered when comparing the fullerenes with planar conjugated systems. Furthermore the use of the HMO ϵ_{LUMO} values cannot explain the relative ease of reduction of C_{60} and C_{70} as C_{70} has a lower lying LUMO than C_{60} whereas their reduction potentials are very similar (Allemand *et al.* 1991; Wudl 1992).

Finally we consider the empirical relationship between electron affinity (EA) and reduction potential ($E_{\frac{1}{2}}$, SCE, aprotic solvents) (Chen & Wentworth 1975)

$$EA = E_{\frac{1}{2}} + 2.49 \pm 0.26 \text{ eV}. \tag{2}$$

Using the experimental reduction potential of C_{60} in (2) leads to a derived EA(C_{60}) of 2.1 eV, much less than the experimental value of 2.65 ± 0.05 eV (Wang *et al.* 1991).

6. Non-planarity and rehybridization

Quite apart from their singular topology, the fullerenes are distinguished from other conjugated hydrocarbons by their non-planarity. The geometrical aspects of fullerene formation as it relates to pyramidalization of the constituent carbon atoms has been recognized for some time (Haddon *et al.* 1986; Haddon 1988). Here we consider the effect of non-planarity on the electronic structure of the carbon atoms as it arises in the fullerenes (Haddon *et al.* 1986; Haddon 1992).

The primary response of a conjugated carbon atom to a deviation from planarity is a rehybridization of the sp^2 σ- and p π-orbitals which are the rule in planar
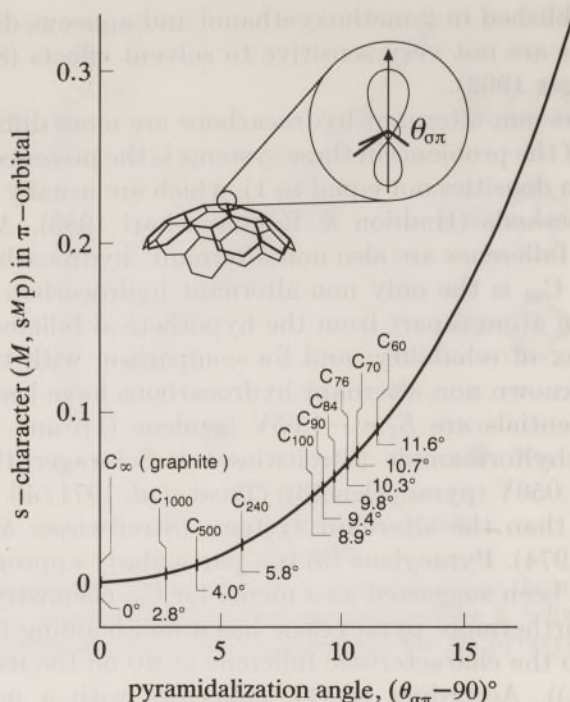
Figure 4. Rehybridization as a function of pyramidalization angle. The π-orbital axis vector (POAV1) approximation), is defined as that vector which makes equal angles to the three σ-bonds at a conjugated carbon atom (Haddon 1988). The common angle to the three σ-bonds (which are assumed to lie along the internuclear axes), is denoted $\theta_{\sigma\pi}$. The average pyramidalization angle $[(\overline{\theta_{\sigma\pi}}-90)°]$ shown for representative fullerenes (C_n), was obtained from eqn (2) of Haddon *et al.* (1986*b*) for $n > 60$.

situations. We have introduced the π-orbital axis vector (POAV) theory to analyse the electronic structure of nonplanar conjugated organic molecules such as the fullerenes (Haddon 1988). The POAV analysis extends σ–π separability into three-dimensions by use of the orbital orthogonality relations that are the basis of standard hybridization theory. In POAV2 theory, a π-orbital is defined as that hybrid orbital that is locally orthogonal to the σ-orbitals, whereas from the standpoint of the POAV1 analysis the π-orbital is that hybrid orbital which makes equal angles ($\theta_{\sigma\pi}$) with the σ-orbitals (figure 4).

Curvature in conjugated organic molecules leads the σ-bonds at the carbon atom to deviate from planarity and there is a change in hybridization: a rehybridization of the carbon atom so that π-orbital is no longer of purely p-orbital character. Thus the fullerenes are of intermediate hybridization (Haddon *et al.* 1986; Haddon & Raghavachari 1992). Using the standard nomenclature, the σ-bond hybridization falls between graphite (sp²) and diamond (sp³). Within certain limits the POAV theories allow a quantitative treatment of the hybridization in non-planar conjugated organic molecules and have been extensively tested (Haddon & Raghavachari 1992). The average POAV1 σ-bond hybridization for C_{60} is $sp^{2.278}$ and the π-orbital fractional s-character is 0.085 (POAV1) and 0.081 (POAV2) (Haddon 1990). The application of the POAV1 theory to the fullerenes takes a particularly simple form and an approximate treatment of the rehybridization required for closure of carbon spheroids of arbitrary size is shown in figure 4 where the curvature of the surface at a carbon atom is expressed by the pyramidalization angle $[(\theta_{\sigma\pi}-90)°]$. A recent

analysis of ^{13}C NMR coupling constants in a derivative of C_{60} led to an estimate of 0.03 for the fractional rehybridization in neutral C_{60} (Hawkins *et al.* 1991; Hawkins 1992).

As may be seen in figure 4 and as noted above for C_{60} the fullerene π molecular orbitals are composed of carbon atomic orbitals which contain a substantial amount of 2s orbital character and as the carbon 2s orbital lies so much lower in energy than the 2p orbital the resulting orbitals are expected to exhibit an enhanced electronegativity when compared with their planar counterparts. Furthermore the fullerenes are not only of intermediate hybridization, but probably exhibit variable hybridization as they pass through different states of reduction, for the pyramidalization of anions is well known. Based on figure 3 it seems that the reduction potential of C_{60} is lowered by about 0.8V as a result of rehybridization effects.

The reductive behaviour of the higher fullerenes (C_n) should be of considerable interest as the 12 5MRs will ensure the presence of low lying energy levels. However, the rehybridization at each carbon atom decreases with increasing values of n and is asymmetrically distributed throughout the molecule for all fullerenes except C_{60} (Haddon & Raghavachari 1992). Furthermore the increasing size of these species will lead to a reduction in electron repulsion and make it easier to ion-pair the negatively charged surface.

7. Conclusion

C_{60} shows an extremely facile reduction profile and there is evidence for the addition of up to 12 electrons to the molecule. The prediction that C_{60} will exhibit an exceptionally high electron affinity and that the molecule will add up to 12 electrons under suitable conditions (Haddon *et al.* 1986a) seems to be borne out by the experimental results. Rehybridization plays an important role in determining the electronic structure of the fullerenes and it is the combination of topology and rehybridization which together account for the extraordinary ability of C_{60} to accept electrons.

References

Allemand, P.-M., Koch, A., Wudl, F., Rubin, Y., Diedrich, F., Alvarez, M. M., Anz, S. J. & Whetten, R. L. 1991 Two different fullerenes have the same cyclic voltammetry. *J. Am. chem. Soc.* **113**, 1050–1051.

Andersen Jr, A. G. & Masada, G. M. 1974 Polarographic reduction potentials of some nonbenzenoid aromatic hydrocarbons. *J. org. Chem.* **39**, 572–573.

Bausch, J. W., Prakash, G. K. S., Olah, G. A., Tse, D. S., Lorents, D. C., Bae, Y. K. & Malhotra, R. 1991 Diamagnetic polyanions of the C_{60} and C_{70} fullerenes: preparation, ^{13}C and ^{7}Li NMR spectroscopic observation, and alkylation with methyl iodide to polymethylated fullerenes. *J. Am. chem. Soc.* **113**, 3205–3206.

Breslow, R. & Grant, J. L. 1977 Electrochemical determination of the basicities of benzyl, allyl, and propargyl anions, and a study of solvent and electrolytic effects. *J. Am. chem. Soc.* **99**, 7745–7746.

Chabre, C., Djurado, D., Armand, M., Romanow, W. R., Coustel, N., McCauley Jr, J. P., Fischer, J. E. & Smith III, A. B. 1992 Electrochemical intercalation of lithium into solid C_{60}. *J. Am. chem. Soc.* **114**, 764–766.

Chen, E. C. M. & Wentworth, W. E. 1975 A comparison of experimental determinations of electron affinities of π-charge transfer complex acceptors. *J. chem. Phys.* **63**, 3183–3191.

Chen, Y., Stepniak, F., Weaver, J. H., Chibante, L. P. F. & Smalley, R. E. 1992 Fullerides of alkaline-earth metals. *Phys. Rev.* B **45**, 8845–8848.

Cox, D. M. *et al.* 1991 Characterization of C_{60} and C_{70} clusters. *J. Am. chem. Soc.* **113**, 2940–2944.

Curl, R. F. & Smalley, R. E. 1988 Probing C_{60}. *Science, Wash.* **242**, 1017–1022.

Dubois, D., Kadish, K. M., Flanagan, S., Haufler, R. E., Chibante, L. P. F. & Milson, L. J. 1991 Spectroelectrochemical study of the C_{60} and C_{70} fullerenes and their mono-, di-, tri-, and tetraanions. *J. Am. chem. Soc.* **113**, 4364–4366.

Dubois, D., Kadish, K. M., Flanagan, S. & Milson, L. J. 1991 Electrochemical detection of fulleronium and highly reduced fulleride (C_{60}^{5-}) ions in solution. *J. Am. chem. Soc.* **113**, 7773–7774.

Fischer, J. E., Heiney, P. A. & Smith III, A. B. 1992 Solid-state chemistry of fullerene-based materials. *Acc. Chem. Res.* **25**, 112–118.

Haddon, R. C. 1988 π-Electrons in three-dimensions. *Acc. Chem. Res.* **21**, 243–249.

Haddon, R. C. 1990 Measure of nonplanarity in conjugated organic molecules: Which structurally characterized molecule displays the highest degree of pyramidalization? *J. Am. chem. Soc.* **112**, 3385–3389.

Haddon, R. C. 1992 Electronic structure, conductivity, and superconductivity of alkali metal doped C_{60}. *Acc. Chem. Res.* **25**, 127–133.

Haddon, R. C. *et al.* 1991 Conducting films of C_{60} and C_{70} by alkali metal doping. *Nature, Lond.* **350**, 320–322.

Haddon, R. C., Brus, L. E. & Raghavachari, K. 1986a Electronic structure and bonding in icosahedral C_{60}. *Chem. Phys. Lett.* **125**, 459–464.

Haddon, R. C., Brus, L. E. & Raghavachari, K. 1986b Rehybridization and π-orbital alignment: the key to the existence of spheroidal carbon clusters. *Chem. Phys. Lett.* **131**, 165–169.

Haddon, R. C., Kochanski, G. P., Hebard, A. F., Fiory, A. T., Morris, R. C. 1992 Electrical resistivity and stoichiometry of Ca_xC_{60} and Sr_xC_{60} films. *Science, Wash.* **258**, 1636–1638.

Haddon, R. C. & Raghavachari, K. 1983 Naphthalene and azulene: theoretical comparison. *J. chem. Phys.* **79**, 1093–1094.

Haddon, R. C. & Raghavachari, K. 1992 Electronic structure of the fullerenes: carbon allotropes of intermediate hybridization, buckminsterfullerenes. *VCH.* (In the press.)

Haufler, R. E. *et al.* 1990 Efficient production of C_{60} (buckminsterfullerene), $C_{60}H_{36}$, and the solvated buckide ion. *J. phys. Chem.* **94**, 8634–8636.

Hawkins, J. M. 1992 Osmylation of C_{60}: proof and characterization of the soccer-ball framework. *Acc. Chem. Res.* **25**, 150–156.

Hawkins, J. M., Loren, S., Meyer, A. & Nunlist, R. 1991 2D nuclear magnetic resonance analysis of osmylated C_{60}. *J. Am. chem. Soc.* **113**, 7770–7771.

Hebard, A. F., Rosseinsky, M. J., Haddon, R. C., Murphy, D. W., Glarum, S. H., Palstra, T. T. M., Ramirez, A. P. & Kortan, A. R. 1991 Superconductivity at 18 K in potassium-doped C_{60}. *Nature, Lond.* **350**, 600–601.

Holczer, K., Klein, O., Huang, S.-M., Kaner, R. B., Fu, K.-J., Whetten, R. L. & Diederich, F. 1991 Alkali-fulleride superconductors: synthesis, composition, and diamagnetic shielding. *Science, Wash.* **252**, 1154–1157.

Kochanski, G. P., Hebard, A. F., Haddon, R. C. & Fiory, A. T. 1992 Electrical resistivity and stoichiometry of K_xC_{60} films. *Science, Wash.* **255**, 184–186.

Kortan, A. R., Kopylov, N., Glarum, S. H., Gyorgy, E. M., Ramirez, A. P., Fleming, R. M., Thiel, F. A. & Haddon, R. C. 1992 Superconductivity at 8.4 K in calcium-doped C_{60}. *Nature, Lond.* **355**, 529–532.

Krätschmer, W., Lamb, L. D., Fostiropoulos, K. & Huffman, D. R. 1990 Solid C_{60}: a new form of carbon. *Nature, Lond.* **347**, 354–358.

Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F. & Smalley, R. E. 1985 C_{60}: Buckminsterfullerene. *Nature, Lond.* **318**, 162–164.

Limbach, P. A., Schweikhard, L., Cowen, K. A., McDermott, M. T., Marshall, A. G. & Coe. J. V. 1991 Observation of the doubly charged, gas-phase fullerene anions C_{60}^{2-} and C_{70}^{2-}. *J. Am. chem. Soc.* **113**, 6795–6798.

Miller, B., Rosamilia, J. M., Dabbagh, G., Muller, A. J. & Haddon, R. C. 1992 Electron transfer to C_{60} and C_{70} fullerenes at hydrodynamic and dual electrodes. *J. electrochem. Soc.* **139**, 1941–1945.

Rosseinsky, M. J. *et al.* 1991 Superconductivity at 28 K in Rb_xC_{60}. *Phys. Rev. Lett.* **66**, 2830–2832.

Saito, S. & Oshiyama, A. 1992 Electronic structure of calcium-doped C_{60}. *Solid State Commun.* **83**, 107–110.

Streitwieser 1962 *Molecular Orbital Theory for organic chemists*, ch. 7. New York: Wiley.

Streitwieser Jr, A. & Schwager, I. 1962 A molecular orbital study of the polarographic reduction in dimethylformamide of unsubstituted and methyl-substituted aromatic hydrocarbons. *J. Am. chem. Soc.* **66**, 2136–2320.

Tanigaki, K., Ebbesen, T. W., Saito, S., Mizuki, J., Tsai, J. S., Kubo, Y. & Kuroshima, S. 1991 Superconductivity at 33 K in $Cs_xRb_yC_{60}$. *Nature, Lond.* **352**, 222–223.

Trost, B. M., Bright, G. M., Frihart, C. & Britelli, D. 1971 Perturbed [12]annulenes. The synthesis of pyracylenes. *J. Am. chem. Soc.* **93**, 737–745.

Wang, L. S., Conceicao, J., Jin, C. & Smalley, R. E. 1991 Threshold photodetachment of cold C_{60}^-. *Chem. Phys. Lett.* **182**, 5–11.

Weaver, J. H. 1992 Fullerenes and fullerides: photoemission and scanning tunneling microscopy studies. *Acc. Chem. Res.* **25**, 143–149.

Wertheim, G. K., Buchanan, D. N. E. & Rowe, J. E. 1992 Charge donation by Ca into the t_{1g} band of C_{60}. *Science, Wash.* **258**, 1638–1640.

Wudl, F. 1992 The chemical properties of buckminsterfullerene (C_{60}) and the birth and infancy of fulleroids. *Acc. Chem. Res.* **25**, 157–161.

Xiang, X.-D., Hou, J. G., Briceno, G., Vareka, W. A., Mostovoy, R., Zettl, A., Crespi, V. H. & Cohen, M. L. 1992 Synthesis and electronic transport of single crystal K_3C_{60}. *Science, Wash.* **256**, 1190–1191.

Xie, Q., Perez-Cordero, E. & Echegoyen, L. 1992 Electrochemical detection of C_{60}^{6-} and C_{70}^{6-}: Enhanced stability of fullerides in solution. *J. Am. chem. Soc.* **114**, 3978–3980.

Yildirim, T., Zhou, O., Fischer, J. E., Bykovetz, N., Strongin, R. A., Cichy, M. A., Smith III, A. B., Lin, C. L. & Jelivek, R. 1992 Intercalation of sodium heteroclusters into the C_{60} lattice. *Nature, Lond.*, **360**, 568–571.

Zhang, Q. L., O'Brien, S. C., Heath, J. R., Liu, Y., Curl, R. F., Kroto, H. W. & Smalley, R. E. 1986 Reactivity of large carbon clusters: spheroidal carbon shells and their possible relevance to the formation and morphology of soot. *J. phys. Chem.* **90**, 525–528.

Discussion

R. E. PALMER (*University of Cambridge, U.K.*). If, hypothetically, you could continue to stretch the spacing in the superconductor, there must come a point where they become insulating again. Is there some theoretical maximum for the T_c that you can envisage?

R. C. HADDON. Cs_3 may represent that point. It seems by the time you get to Cs_3 the spacing between the balls that is necessary to accommodate Cs becomes too large. I don't know if it is an argument for the electronic structure of the material, although it always seems that superconductors are on the verge of some sort of instability. I don't know of any theoretical maximum in terms of the T_c, but I think as you start to move the balls apart, the band width will get so narrow that localization will develop.

H. W. KROTO (*University of Sussex, U.K.*). Is there anything special about the number 3, or does no one know? Should one be looking for another fullerene which has maybe, double degeneracy?

R. C. HADDON. I think there is something special. We do need more fullerenes with triply degenerate orbitals; unfortunately none have been isolated beside C_{60}. It comes about as a result of the direct product of the t-type orbitals.

P. A. SERMON (*Brunel University, U.K.*). Does your doping procedure only involve alkali metals or is there oxygen involved?

R. C. HADDON. We don't believe that there is any oxygen involved.

P. A. SERMON. May I take it that this type of superconductivity is quite different from that of the ceramics that have been described in the literature?

R. C. HADDON. I think so. The explanation that I have mentioned seems to be fairly successful in accounting for the result. It is based on vibrations, even though they are molecular vibrations. As far as I know, there is no accepted theory of super-conductivity in ceramics. In fact, that is one of the uses we can point to for C_{60} superconductors. I think that, in the end, these will be among the best understood of the superconductors.