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Generation and hydrogenation of adjacent-pentagon fullerenes: astrochemical considerations

Simon Petrie and Diethard K. Bohme

Department of Chemistry and Centre for Research in Earth and Space Science, York University, North York, Ontario, Canada M3J 1P3

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ABSTRACT

Recent theories advanced to account for diffuse interstellar (IS) bands and for several other IS spectral features have included as postulated carriers of these features the fullerene molecule C_{60} and its hydrogenated analogues. We propose that the most likely sites of hydrogenation upon a fullerene under IS conditions are at adjacent 'defects' which are present upon the carbon surfaces of some fullerenes. C–H and C–C bonds associated with such sites are expected to exhibit substantially different spectral characteristics to those bonds at other sites. Hydrogenation of these adjacent-pentagon 'defect' sites also provides a plausible mechanism for the stabilization of fullerenes smaller than C_{60}, which might reasonably be expected to accompany the circumstellar generation of larger fullerenes.

Key words: molecular processes – circumstellar matter – ISM: clouds – ISM: molecules.

1 INTRODUCTION

The possible presence of fullerenes in the interstellar medium has been a topic of continued debate in the astrophysical community since the discovery (Kroto et al. 1985) and subsequent synthesis (Krätschmer et al. 1990) of these carbon cage molecules. Hare & Kroto (1992) have suggested that the conditions encountered in laboratory generation of the fullerenes – most often employing a high-temperature plasma of carbon and helium – are broadly similar to those encountered in the envelopes of giant, mass-losing H-deficient, C-rich stars such as R Corona Borealis (O'Keefe 1939). Other researchers have proposed that fullerenes may exist within circumstellar and/or interstellar environments as neutral molecules (Kroto et al. 1985), as positive ions (Léger et al. 1988; Javahery et al. 1992; Miller 1992) or negative ions (Millar 1992), as charge-transfer complexes with metal ions (Kroto & Jura 1992), as exohedral or endohedral complexes of various substituents (Heymann 1986; Ballester, Antoniewicz & Smoluchowski 1990), as hydrogenated molecules (Webster 1991) or ions (Petrie et al. 1992), as derivatized ions (Bohme 1992; Petrie, Javahery & Bohme 1992), or as constituents of nuclei of interstellar dust grains (Kroto 1989; Balm & Kroto 1990). Debate still proceeds as to which of these forms is most probable, and whether fullerenes do indeed exist within interstellar (IS) and circumstellar (CS) environments: initial searches for C_{60} within astrophysical environments have proved unsuccessful (Snow & Seab 1989; Somerville & Bellis 1989). Recently, Webster (1992, 1993a,b,c) has explored in detail the theory that variously hydrogenated fullerenes, also called fulleranes, are the carriers of the diffuse IS bands and of other IS and CS spectral features.

Almost all of the debate concerning the possible presence of fullerenes within the interstellar medium has been restricted to C_{60} or to direct chemical derivatives of C_{60}. In some instances this focus has arisen from reasons of computational simplicity – C_{60} is the smallest fullerene to have been isolated in macroscopic quantities and possesses a substantially greater degree of symmetry than almost all other fullerenes. Often, however, the astrochemical preoccupation with C_{60} appears to reflect an implicit assumption that C_{60} will be the most abundant IS or CS fullerene for the same reasons that underlie its dominance in the laboratory generation of fullerenes. Here we provide a critical assessment of this assumption.

2 STRUCTURE AND GEOMETRY OF THE FULLERENE SURFACE

Several aspects of fullerene structure are dictated by geometrical considerations. For example, it can be shown that closure of a carbon network is possible only if the network contains an even number of carbon atoms; and, provided that the network comprises only pentagonal and hexagonal carbon rings, the structure must possess exactly 12 pentagons (Kroto 1987). From these and other requirements it is possible to determine that, upon the surface of a given fullerene, each C atom must fall into one of the four categories shown in Fig. 1. In practice, only [C_5, C_6, C_6] and [C_6, C_6, C_6] structural features have been observed in fullerenes isolated in laboratory studies (Diederich & Whetten 1992; Smalley 1992), and [C_5, C_5, C_5] features are expected to exist only within very small fullerenes and within very narrow-diameter 'buckytubes'. Buckminsterfullerene, C_{60}, is unique in possessing only one type of structural feature, namely, [C_5, C_6, C_6].

With regard to energetic factors, all fullerenes possess some degree of strain induced by the curvature of the carbon surface, and so all fullerenes are thermodynamically unstable with regard to graphite. For a given number of carbon atoms, the instability can be minimized in the structure that possesses the greatest uniformity of curvature. This trend is, to some extent, embodied in the 'isolated-pentagon rule' (Smalley 1992) which arises from the observation that [C_5, C_5, C_5] and [C_5, C_5, C_6] structural features – that is, those features involving adjacent pentagons, and which possess a high degree of local curvature – are not observed in fullerenes isolated in macroscopic quantities.

3 LABORATORY STUDIES OF FULLERENE GENERATION

Carbon clusters produced by the laser or 'contact arc' vaporization of graphite often show a local maximum in their mass spectra at m/z 720, arising from $C_{60}^{\bullet +}$.

The identification of this cluster as a fullerene by Kroto et al. (1985) preceded rigorous structural determination but has since been amply confirmed by other techniques. Another, generally less intense, 'magic number' peak is observed at m/z 840 (C_{70}).

The mechanism of fullerene formation is still uncertain, and several pathways have been considered (Smalley 1992; Curl 1993): the proposal that has received the most attention recently (von Helden, Gotts & Bowers 1993a; von Helden et al. 1993b; Hunter, Fye & Jarrold 1993a,b) is that fullerenes result from the isomerization of large, planar initially monocyclic carbon molecules or ions. This isomerization or 'annealing' process is estimated to have associated with it a considerable activation energy barrier [of approximately 3.7 eV for conversion of monocyclic rings, in the C_{50}–C_{70} size range, to the corresponding fullerenes (Hunter et al. 1993b)] and so can only proceed efficiently at elevated temperatures. Evidence is also mounting (Chibante et al. 1993) that fullerene formation is impeded by intense UV irradiation often associated with the carbon arc technique employed in laboratory fullerene synthesis.

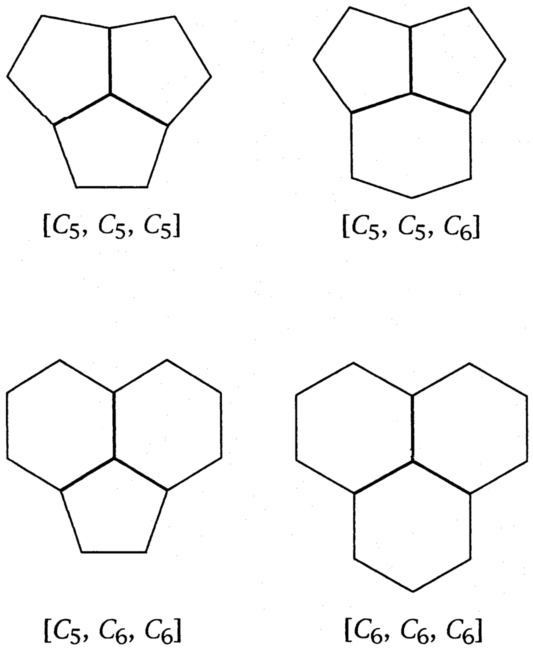
[C_5, C_5, C_5]
[C_5, C_5, C_6]
[C_5, C_6, C_6]
[C_6, C_6, C_6]

Figure 1. The four different elements of fullerene geometry, as defined by the polygons associated with a surface C atom.

With regard specifically to C_{60}, its initial reported predominance in laboratory fullerene samples was later found to reflect something of a bias in the solubility of fullerenes within the solvent employed, toluene. Later studies have shown that, while C_{60} may still be the single most abundant carbon cluster within most samples, the combined yield of higher-molecular-weight fullerenes (C_{120} to at least C_{360}) is also considerable under certain conditions. These larger fullerenes dissolve sparingly in toluene but are considerably more soluble in higher-boiling-point solvents such as 1,2,4 trichlorobenzene (Diederich et al. 1991). Isolation of specific fullerenes larger than about C_{100} has, to date, been thwarted largely by the existence of several stable isomers for many of these clusters and by the difficulty in separating out such chemically similar clusters (Diederich & Whetten 1992). The preponderance of C_{60} has been taken to indicate a kinetic preference for formation and stabilization of this cluster, but does not indicate a thermodynamic trend: C_{70}, which is almost always formed in substantially lower yield than C_{60}, has a lower heat of formation per carbon atom (Zhang, Wang & Ho 1992), and the coagulation of two C_{60} molecules to form C_{120} and related molecules under conditions of high temperature and pressure (Yeretzian et al. 1992) is calculated to be exothermic by up to 20 eV (Adams et al. 1992). The tendency for formation of relatively large amounts of C_{60} in laboratory experiments appears to result from the unique position of this carbon cluster as the smallest 'isolated-pentagon' fullerene. Smaller fullerenes, which must feature at least one pair of adjacent pentagons, have not been isolated in the solid state although they are observable in the gas phase immediately following cluster formation (Smalley 1992). A justification for the apparent instability of fullerenes smaller than C_{60} in the solid state is that the adjacent-pentagon feature induces comparatively poor π overlap in the atomic orbitals that are perpendicular to the local carbon surface. Associated with this poor overlap is the expectation that the orbitals concerned (which are considered to possess both sp^2 and sp^3 character, with rather more sp^3 character than is found in the analogous orbitals associated with [C_5, C_6, C_6] and [C_6, C_6, C_6] features) will display a greater readiness to form chemical bonds with atoms outside of the fullerene carbon cage. In this regard, we have recently observed evidence for this in the substantially heightened reactivity of the small fullerene ions C_{56}^{n+} and C_{58}^{n+} ($n=1, 2$) (Petrie & Bohme 1993). It seems reasonable to suppose that some of the local overabundance of C_{60} observed in laboratory synthesis arises from the chemical instability of bare, adjacent-pentagon fullerenes and is perhaps mediated by C_n switching reactions in the gas phase; for example,

$$C_{58} + C_{64} \longrightarrow C_{60} + C_{62}, \qquad (1)$$

$$C_{62} + C_{62} \longrightarrow C_{60} + C_{64}, \qquad (2)$$

or by similar disproportionation reactions in the solid carbonaceous deposits formed in the cooler regions of the reaction vessel. Alternatively, Diederich and coworkers have suggested that a preponderance of C_{60} is due to the low reactivity of C_{60} with regard to gas-phase coalescence reactions; these coalescence reactions, for example,

$$C_{56} + C_{62} \longrightarrow C_{116} + C_2, \qquad (3)$$

permit the growth of larger fullerenes from smaller unstable clusters. This proposal is consistent with the observed lack of small clusters other than C_{60} and C_{70} and with the relatively high abundances seen for clusters larger than C_{100} (Diederich et al. 1991; Yeretzian et al. 1992).

The effect of reactive contaminants upon fullerene formation is not accurately known, and it is widely considered that such contamination impedes fullerene synthesis; however, fullerenes have been formed within sooting flames (Gerhardt, Löffler & Homann 1987; Howard et al. 1992), by laser vaporization of polycyclic aromatic hydrocarbons (So & Wilkins 1989), and by the photolysis of large, polyoxygenated organic molecules (Rubin et al. 1991; McElvany et al. 1993) so that the presence of some hydrogen and/or oxygen in the clustering gas does not totally preclude fullerene generation.

4 CIRCUMSTELLAR GENERATION OF FULLERENES

The possible CS generation of fullerenes is dependent upon many factors: particle density, temperature, radiation flux, rate of radiative emission of the various cluster precursors, rate of gas outflow within the CS envelope, reaction sequence leading to fullerene formation, degree of ionization and elemental composition of the CS composition, to name some of the more obvious criteria. At present the quantitative effect of any of these factors upon fullerene formation is simply not known; however, there are general qualitative considerations that can be presented.

It is important to realize that C_{60} will not necessarily remain the most abundant fullerene in significantly contaminated carbon gas mixtures, and CS envelopes must surely be considered in this category rather than as the pure helium/carbon plasmas characteristic of laboratory fullerene synthesis. The most promising candidates for CS fullerene production include the R CrB stars, which are extremely underabundant in hydrogen. The chemical compositions of the atmospheres of the stars R Corona Borealis and XX Camelopardalis have been reported by Cottrell & Lambert (1982) and are summarized here in Table 1. It can be seen from this tabulation that carbon is the most abundant chemically reactive element in the atmospheres of these R CrB stars. If it is assumed that fullerene formation proceeds initially from atomic reactants that are reasonably well mixed within the atmosphere, then the production of, for example, buckminsterfullerene, C_{60}, requires at least 59 two-body collisions between carbon atoms or molecules. The elemental abundances for R CrB and XX Cam indicate that any such reaction sequence will also feature collisions with atomic oxygen and atomic nitrogen (even if most of the N and O does become locked up as CN and CO), and that for R CrB at least, collisions with atomic hydrogen are also somewhat probable. The effect of these contaminants upon the course of carbon clustering in circumstellar envelopes is not known, but is likely to allow access to alternative pathways in competition with those possible in the presence only of carbon and helium.

Stars such as as R CrB and XX Cam represent one end of the continuum of observed stellar hydrogen abundances; a much larger population of mass-losing, less hydrogen-deficient stars also exists. If stars possessing a larger abundance of hydrogen are also possible sources of fullerenes, then it is of interest to examine the possible effects of hydrogen upon the CS synthesis of fullerenes.

5 FULLERANES: FORMATION AND STABILITY

One plausible effect arising from the presence of atomic hydrogen is a reduction in the difference in stability between adjacent-pentagon and isolated-pentagon fullerenes, since much of this difference appears to arise from the chemical reactivity of adjacent-pentagon sites: formation of a fullerane with the adjacent-pentagon sites hydrogenated may well serve to deactivate these sites. We have previously reported the tendency of the fullerene ions $C_{60}^{\bullet +}$, C_{60}^{2+}, $C_{70}^{\bullet +}$ and C_{70}^{2+} to add atomic hydrogen repeatedly in the gas phase at 294 K (Petrie et al. 1992); the repeated addition of $H^{\bullet}$ to neutral C_{60} has also been noted in the gas phase (Attalla et al. 1993) at elevated temperatures (673 K) and pressures (~ 65 atm), and in solid-state, matrix isolation studies (Howard 1993). We have recently also obtained evidence (Bohme et al., in preparation) that $C_{58}^{\bullet +}$, an 'adjacent-pentagon' fullerene ion, is at least as efficient as $C_{60}^{\bullet +}$ at adding hydrogen atoms. We anticipate that the C–H bond will be stronger for an adjacent-pentagon C atom than for a C atom not involved in the junction of two pentagons. While there is no direct evidence that this is generally the case, we can consider the differences in enthalpies of dihydrogenation for the polyhedral molecules C_{60} (all carbon atoms of the type $[C_5, C_6, C_6]$) and $C_{60}H_{18}$ (all C atoms of the type $[C_5, C_5, C_5]$):

$$C_{60} + H_2 \longrightarrow C_{60}H_2 \qquad -\Delta H_4^0 = 35.6\ \mathrm{kcal\ mol^{-1}} \qquad (4)$$

$$C_{20}H_{18} + H_2 \longrightarrow C_{20}H_{20} \qquad -\Delta H_5^0 = 64 \pm 3\ \mathrm{kcal\ mol^{-1}}. \qquad (5)$$

These values may not be strictly comparable, since the value for equation (4) was obtained by PM-3 force field calculations (Matsuzawa, Dixon & Fukunaga 1992) while $-\Delta H_5^0$ represents an experimental value obtained by ion/molecule bracketing studies (Kiplinger et al. 1989). Nevertheless, experimental studies show that $C_{60}H_2$ and more highly hydrogenated fulleranes are prone to dehydrogenation at ~ 600 K (Rüchardt et al. 1993; Banks et al. 1993), while a much greater degree of thermal stability has been observed for dodecahedrane, $C_{20}H_{20}$ (Paquette 1989). If both of the above enthalpies of hydrogenation are accurate, these values indicate that a C–H bond in the all-$[C_5, C_5, C_5]$ carbon cage

Table 1. Atmospheric compositions of the R CrB stars R Corona Borealis and XX Camelopardalis, from Cottrell & Lambert (1982).

Element	n(R CrB)^{a,b}	n(XX Cam)^{a,b}	n(solar)^{a,c}
H	0.015	$< 3 \times 10^{-5}$	12500
He	1000	1000	1000
C	4	3	5
N	0.6	1.4	1.5
O	1.6	1.9	8
Fe	0.08	0.01	0.3

Notes: ^{a}elemental abundance on a scale noramlized to n(He) = 1000; ^{b}values for R Corona Borealis and XX Camelopardalis, from Cottrell & Lambert (1982); ^{c}solar photospheric values, from Trimble (1975).

compound $C_{20}H_{20}$ is approximately 15 kcal mol^{-1} stronger than that in the all-$[C_5, C_6, C_6]$ fullerene C_{60} and its fullerane analogues. This difference in bond strength is considerable and suggests that, in general, the dissociation of an adjacent-pentagon C–H bond requires substantially more energy (e.g. a more energetic UV photon) than dissociation of an isolated-pentagon C–H bond. If it is assumed also that migration of hydrogen atoms upon the fullerene/fullerane surface is possible under IS or CS conditions, such migration is likely to lead to preferential hydrogenation at those sites having the highest C–H bond strength – that is, the $[C_5, C_5, C_5]$ or $[C_5, C_5, C_6]$ sites if the fullerene possesses such sites. It follows also that, since the energy required for thermal or photodissociative dehydrogenation of a C–H bond will increase in the order $[C_6, C_6, C_6] < [C_5, C_6, C_6] < [C_5, C_5, C_6] < [C_5, C_5, C_5]$, the strongest C–H bonds should also be the longest-lived under IS or CS conditions.

Our studies of fullerene ion/molecule astrochemistry (Bohme 1992; Petrie et al. 1993) have indicated that few, if any, chemical processes exist for the destruction or fragmentation of the fullerene cage under IS cloud conditions. However, we have suggested (Bohme et al., in preparation) that cosmic-ray (c.r.) ionization of IS fullerenes may be accompanied by the loss of C_2 units,

$$C_{60} + \text{c.r.} \longrightarrow C_{60}^{n+} + ne + \text{c.r.}' \qquad (6a)$$

$$\longrightarrow C_{58}^{n+} + C_2 + ne + \text{c.r.}' \qquad (6b)$$

$$\longrightarrow C_{60-2m}^{n+} + C_{2m} + ne + \text{c.r.}' \qquad (6c)$$

where ne denotes the number of electrons, by comparison with the experimentally observed tendency for fullerene fragmentation to proceed by C_2 loss. The cosmic-ray processing of C_{60} and larger fullerenes within the interstellar medium thus appears likely to provide another source for adjacent-pentagon fullerenes, in an environment where atomic hydrogen is generally one of the most abundant species.

6 DISCUSSION

The arguments that we have presented above suggest that fullerenes possessing adjacent pentagons will tend to undergo preferential hydrogenation at these adjacent-pentagon sites and will tend to maintain a higher level of hydrogenation than fullerenes lacking adjacent pentagons. Furthermore, the presence of hydrogen in the carbon-clustering region of a circumstellar envelope will tend to favour the production and stabilization of fullerenes featuring adjacent pentagons. Therefore the use only of C_{60} and its fulleranes (or of other hydrogenated isolated-pentagon fullerenes), in calculations aimed at understanding the observed diffuse IS bands and other IS spectral features, may fail in several important respects to model these features. We recommend strongly that models involving adjacent-pentagon fulleranes should also be investigated.

While there is no necessity, as we have discussed here, for the CS generation of fullerenes to parallel closely the laboratory generation of fullerenes in high-temperature carbon/helium mixtures, it is noteworthy that the most abundant carbon cluster produced in these experiments is the smallest (C_{60}) that is stable under laboratory conditions. If this trend is operative also in CS fullerene production, a consequence may be that the presence of hydrogen in the clustering region will tend to reduce the size of the fullerenes produced; for example, the most abundant clusters may be hydrogenated clusters in the size range C_{50}–C_{58}, rather than C_{60}. In this respect, we note that Kroto and coworkers (Allaf et al. 1992) have recently performed preliminary studies upon the generation of C_{10}–C_{40} carbon clusters in H_2/He mixtures, and have noted:

(i) a reduction in the efficiency of fullerene generation; and

(ii) a trend towards production of smaller, hydrogenated clusters (presumably fulleranes), with increasing H_2:He ratios.

This observation appears to provide some support for our contention that the presence of hydrogen is likely to favour adjacent-pentagon fullerene (and fullerane) formation in CS envelopes.

Experimental or theoretical verification of this conjecture is liable to prove difficult. A comparison of the frequencies of observed DIB with those of the infrared-active vibrational modes of adjacent-pentagon fulleranes (such as $C_{58}H_6$) and isolated-pentagon fulleranes (such as $C_{60}H_6$) would prove informative. Webster (1993c) has performed force-field calculations to estimate the infrared spectra of $C_{60}H_{60}$ (a fully hydrogenated isolated-pentagon fullerene) and $C_{20}H_{20}$ (a fully hydrogenated, all-$[C_5, C_5, C_5]$ fullerene), and has claimed generally close matches between the calculated vibrational modes of $C_{60}H_{60}$ and several observed DIBs. Interestingly, the DIBs correlated by Webster with C–H-rocking and C–H-stretching features in the calculated spectrum of $C_{60}H_{60}$ are also virtually coincident with the C–H-rocking and C–H-stretching features, at 7.70 and 3.40 μm, respectively, in the experimental infrared spectrum of $C_{20}H_{20}$ (Paquette et al. 1983). While we do not contend that $C_{20}H_{20}$ is a probable IS or CS fullerane, the comparison of $C_{60}H_{60}$ and $C_{20}H_{20}$ does suggest that some DIB features can be matched by a wide variety of candidate molecules. Furthermore, it appears from the calculated spectra of $C_{20}H_{20}$ and $C_{60}H_{60}$ that the most useful features, in terms of identifying the DIB carrier as an adjacent-pentagon or isolated-pentagon fullerane, are likely to be features due to C–C vibrational modes – since the fundamental difference between adjacent-pentagon and isolated-pentagon fulleranes is in the connectivity of their respective carbon skeletons.

Finally, it is not apparent whether Webster's comparison of calculated (Webster 1993c) and observed (Paquette et al. 1983) spectral features for $C_{20}H_{20}$ as a method of assessing the reliability of similar calculations for $C_{60}H_{60}$ (for which no experimental spectral data are available) is valid: the dodecahedral $C_{20}H_{20}$ molecule possesses virtually no angle strain, while the cumulative angle strain in fully externally hydrogenated $C_{60}H_{60}$ is very large (Guo & Scuseria 1992), and is ignored in the force-field calculation employed by Webster. Higher level calculations may permit consideration of the effects of angle strain, but such calculations, especially for the low-symmetry fulleranes that are likely to be of interstellar interest, may well be very computationally intensive. Alternatively, the experimental determination of infrared spectra for laboratory-isolated fulleranes would be of much use in assessing the observed DIB, but isolation of any fullerane possessing fewer than 60 carbon atoms (with the exception of the 'special case' of dodecahedrane, $C_{20}H_{20}$) has not yet been reported and is likely to prove difficult. Nevertheless, we recommend comparison of the expected spectral features arising in adjacent-pentagon and isolated-pentagon fulleranes as an important aspect in determining the nature of the carrier(s) of the diffuse interstellar bands.

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REFERENCES

Adams G. B., Sankey O. F., Page J. B., O'Keefe M., Drabold D. A., 1992, Science, 256, 1792

Allaf A. W., Hallett R. A., Balm S. P., Kroto H. W., 1992, Int. J. Mod. Phys., B6, 3595

Attala M. I., Vassallo A. M., Tattam B. N., Hanna J. V., 1993, J. Phys. Chem., 97, 6329

Ballester J. L., Antoinewicz P. R., Smoluchowski R., 1990, ApJ, 356, 507

Balm S. P., Kroto H. W., 1990, MNRAS, 245, 193

Banks M. R. et al., 1993, J. Chem. Soc., Chem. Commun., 1149

Bohme D. K., 1992, Chem. Rev., 92, 1487

Chibante L. P. F., Thess A., Alford J. M., Diener M. D., Smalley R. E., 1993, J. Phys. Chem., 97, 8696

Cottrell P. L., Lambert D. L., 1982, ApJ, 261, 595

Curl R. F., 1993, Nat, 363, 14

Diederich F., Whetten R. L., 1992, Accounts Chem. Res., 25, 119

Diederich F. et al., 1991, Sci, 252, 548

Gerhardt Ph., Löffler S., Homann K. H., 1987, Chem. Phys. Lett., 137, 306

Guo T., Scuseria G. E., 1992, Chem. Phys. Lett., 191, 527

Hare J. P., Kroto H. W., 1992, Accounts Chem. Res., 25, 106

Heymann D., 1986, J. Geophys. Res., 91, E135

Howard J. A., 1993, Chem. Phys. Lett., 203, 540

Howard J. B., McKinnon J. T., Johnson M. E., Makarovsky Y., Lafleur A. L., 1992, J. Phys. Chem., 96, 6657

Hunter J., Fye J., Jarrold M. F., 1993a, J. Phys. Chem., 97, 3460

Hunter J., Fye J., Jarrold M. F., 1993b, Science, 260, 784

Javahery G., Petrie S., Wang J., Bohme D. K., 1992, Chem. Phys. Lett., 195, 7

Kiplinger J. P., Tollens F. R., Marshall A. G., Kobayashi T., Lagerwall D. R., Paquette L. A., Bartmess J. E., 1989, J. Am. Chem. Soc., 111, 6914

Krätschmer W., Lamb L. D., Fostiropoulos K., Huffmann D. R., 1990, Nat, 347, 354

Kroto H. W., 1987, Nat, 329, 529

Kroto H. W., 1989, Ann. Phys. (Paris), 14, 169

Kroto H. W., Jura M., 1992, A&A, 263, 275

Kroto H. W., Heath J. R., O'Brien S. C., Curl R. F., Smalley R. E., 1985, Nat, 318, 162

Léger A., d'Hendecourt L., Verstraete L., Schmidt W., 1988, A&A, 203, 145

McElvany S. W., Ross M. M., Goroff N. S., Diederich F., 1993, Science, 259, 1594

Matsuzawa N., Dixon D. A., Fukunaga T., 1992, J. Phys. Chem., 96, 7594

Millar T. J., 1992, MNRAS, 259, 35P

O'Keefe J. A., 1939, ApJ, 90, 294

Paquette L. A., 1989, Chem. Rev., 89, 1051

Paquette L. A., Ternansky R. J., Balogh D. W., Kentgen G., 1983, J. Am. Chem. Soc., 105, 5446

Petrie S., Bohme D. K., 1993, Nat, 365, 426

Petrie S., Javahery G., Wang J., Bohme D. K., 1992, J. Am. Chem. Soc., 114, 6268

Petrie S., Javahery G., Bohme D. K., 1993, A&A, 271, 662

Rubin Y., Kahr M., Knobler C. B., Diederich F., Wilkins C. L., 1991, J. Am. Chem. Soc., 113, 495

Rüchardt C. et al., 1993, Agnew. Chem. Int. Ed. Engl., 32, 584

Smalley R. E., 1992, Accounts Chem. Res., 25, 98

Snow T. P., Seab C. G., 1989, A&A, 213, 291

So H. Y., Wilkins C. L., 1989, J. Phys. Chem., 93, 1184

Somerville W. B., Bellis J. G., 1989, MNRAS, 240, 41P

von Helden G., Gotts N. G., Bowers M. T., 1993a, Nat, 363, 60

von Helden G., Hsu M.-T., Gotts N. G., Bowers M. T., 1993b, J. Phys. Chem., 97, 8182

Webster A., 1991, Nat, 352, 412

Webster A. S., 1992, A&A, 257, 750

Webster A. S., 1993a, MNRAS, 262, 831

Webster A. S., 1993b, MNRAS, 263, 385

Webster A. S., 1993c, MNRAS, 264, 121

Yeretzian C., Hansen K., Diederich F., Whetten R. L., 1992, Nat, 359, 44

Zhang B. L., Wang C. Z., Ho K. M., 1992, Chem. Phys. Lett., 193, 225