

Trends in Chemistry

Endohedral fullerene research

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(Received July 14th, 1994)

Abstract. Research on endohedral fullerenes has yielded unambiguous evidence for the existence of selected inside-the-cage complexes. Milligram quantities of purified samples of metallofullerenes have been produced, and characterized via techniques that selectively probe the endohedral guest. Experiments aimed at a detailed understanding of the molecular properties of the endohedral complexes as well as of the material properties of compounds containing endohedral fullerenes have just started.

Introduction

In 1985 Kroto, Heath, O'Brien, Curl, and Smalley, inspired by the work of the architect R. Buckminster Fuller, realized that there was a most elegant solution to the problem of explaining the extraordinary stability observed for the 60 atom all-carbon clusters¹. The solution proposed was the symmetrical arrangement known as the soccerball pattern – a truncated icosahedron consisting of 12 pentagons and 20 hexagons – dubbed Buckminsterfullerene. The experimental evidence required to substantiate this intuitive leap proved difficult to obtain, however, and it was only in 1990 that this became possible when Krätschmer, Lamb, Fostiropoulos, and Huffman² reported a simple technique to produce and purify macroscopic amounts of these molecules. The C₆₀ molecule is only the prototype of a whole new class of stable carbon molecules, all consisting of hollow cages composed of a network of carbon atoms arranged to form 12 pentagons and a varying number of hexagons, the class of the fullerenes. Immediately after production of fullerenes in macroscopic amounts appeared feasible, physicists, material scientists and chemists joined forces in an explosion of effort to unravel a large number of stable fullerene structures, and to investigate properties of fullerenes and fullerene based materials.

Fullerenes show interesting dynamics in the solid state; due to the (nearly) spherical symmetry and the weak van der Waals interactions between the fullerenes in the crystalline phase there is a large degree of rotational freedom, leading to novel rotational ordering transitions³ and interesting accompanying changes in the electronic and optical spectra. Intercalation compounds of C₆₀ with a variety of first and second row alkali earth metals that have superconducting properties have been produced⁴ whereas the same C₆₀ material can also be doped to produce the highest temperature organic ferromagnet currently known^{5,6}. In addition, fullerenes serve as building blocks in a new branch of three-dimensional chemistry⁹.

After the discovery of the fullerenes it was realised and experimentally demonstrated that similar cage-structures

can explain the observations of magic numbers in the abundance spectra of other metal-carbon clusters⁷. More recently, theoretical calculations on the geometrical structure of silicon clusters have revealed structures that are formed by two shells of atoms, the outer one (cage) being fullerene-like and the inner one (core) consisting of a few atoms saturating dangling bonds⁸. These calculations support the experimental observations that selected silicon clusters, most notably Si₄₅, are (somewhat) less reactive than silicon clusters containing a few silicon atoms more or less.

Apart from doping *in between* fullerene-molecules, as in the aforementioned intercalation compounds, doping of the fullerenes can also be performed by substituting carbon atoms in the shell for foreign atoms, as in C₅₉B for instance. These latter compounds have been produced and detected in molecular beam experiments but appear to be too reactive to survive ambient conditions¹⁰. The most intriguing way of doping the fullerenes is by producing 'inside-the-cage' complexes, the so-called endohedral (from Greek: *endon* = within, *hedra* = face of a geometrical form) fullerenes. Fullerenes have the capability of encapsulating other atoms or even small molecules in the 4 Å diameter hollow void. The nomenclature A@C_n is used to indicate that a species A is inside a C_n fullerene cage¹⁰.

Endohedral fullerenes

Endohedral fullerenes are predicted to have interesting properties on the molecular level. If a metal atom like Na is enclosed, it will donate its valence electron to the fullerene cage, and a complex best described as Na⁺@C₆₀⁻ is formed. The sodium ion will possess an equilibrium position away from the center of the cage. The system thereby acquires a large dipole moment which interacts favorably with the polarizable electron density of the fullerene cage. Potential energy calculations show that distribution of the alkali ion in the C₆₀-shell is essentially spherically symmetrical. The cationic potential energy sur-

face has similarities with the energy surface used in the description of a diatomic molecule, and the motion of the ion in the cage can be described using an inverted Morse potential; there is large repulsion at the cage wall, whereas there is a small barrier toward motion through the center of the cage. The vibrational motion has a characteristic frequency around 100 cm^{-1} ; the free rotation of the ion about the center of mass of the ion-cage complex has a rotational constant of 1 cm^{-1} associated with it. The rotation-vibration spectrum of a complex like $\text{Na}@C_{60}$ should have, therefore, a wealth of strong IR active lines in the $1\text{--}500\text{ cm}^{-1}$ part of the spectrum^{11,12}. It appears, therefore, that endohedral fullerenes enable a study of the rattling motion of the world's smallest rattle.

Endohedral fullerenes are expected to serve as building blocks for materials with exciting properties. Calculations indicate that electric, like magnetic, dipoles inside a fullerene cage will only be partially screened. This, together with the free rotation of the dipoles within the cage, opens the possibility for the experimental realization of an ideal electric dipolar and an ideal magnetic dipolar lattice¹³. As the dipole-dipole interaction between endohedral fullerenes is rather weak, it is expected that the packing of endohedral fullerenes in the solid is similar to the packing of the undoped fullerenes. For endohedral C_{60} this implies that at high temperatures, where rapid rotations smear out any detail of the faceted shape of the molecules, a fcc crystal structure will exist. If the temperature is reduced, the molecules will still occupy the same lattice sites but orientational order will develop in the crystal. The screening of the internal dipole moments by the C_{60} cage is isotropic and insensitive to rotations of the cage, however. One can therefore use the picture of (otherwise free) interacting dipoles on a fcc lattice to describe the thermodynamics associated with the dipolar interaction. Such a dipolar lattice of the fcc type is expected to undergo a transition to a low-temperature dipole-oriented phase, a conjecture that has to be experimentally investigated.

First experimental evidence for the existence of endohedral fullerenes dates back to molecular beam experiments in 1985. In these experiments, endohedral complexes were made by laser vaporization of an intercalated graphite rod and detected via laser-ionization and mass-selective detection. Photofragmentation studies provided strong evidence that the guest atoms were *inside* the cage¹⁴. After the Krätschmer-Huffman discovery it was realized that the efficiency of (endohedral) fullerene production in these laser vaporization experiments can be increased by orders of magnitude if vaporization is performed at elevated temperatures. In 1991 it was indeed shown that laser vaporization of intercalated graphite in a hot (1200°C) inert gas flow can be used for macroscopic production of endohedral fullerenes. An even simpler approach to the production of macroscopic quantities of endohedral fullerenes is to use arc vaporization of a composite rod made of graphite and the metal, or the oxide of it, to be encapsulated. In 1992 Johnson et al.¹⁵ reported that milligram quantities of $\text{La}@C_{82}$ can be produced in this way and recorded the EPR spectrum of the complex, the unambiguous evidence for the existence of the endohedral fullerene. Since then endohedral fullerenes with various atoms and even small molecules inside have been produced. Under optimum conditions the yield of endohedral fullerenes relative to the empty ones can exceed 1%.

Although a large number of endohedral fullerene complexes have been produced and subsequently detected via mass-spectrometric techniques, the production of high purity samples of endohedral fullerenes in sufficient amounts, and most notably of endohedral C_{60} samples, is a major challenge. Experimental progress has been hampered by difficulties encountered in separating endohedral fullerenes from the soot, from other fullerenes and from other endohedral complexes. Up to now solvent extraction of endohedral complexes from the soot followed by sequential high performance liquid chromatographic (HPLC) separation has been successfully used for

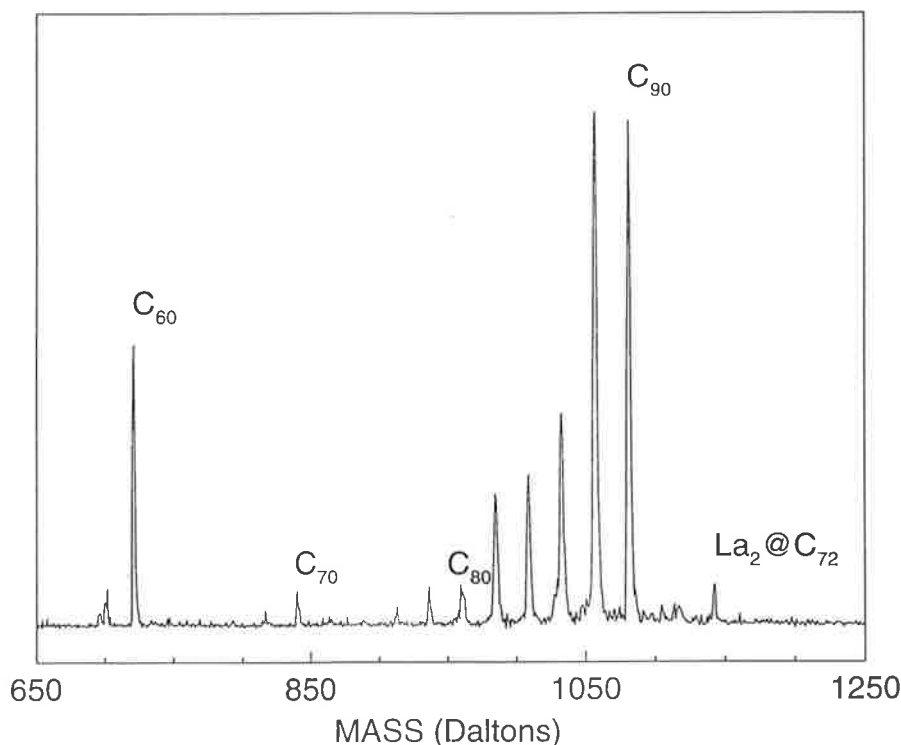


Figure 1. Laser Desorption Post-Ionization Time-Of-Flight Mass spectrum (mass resolution $m/\Delta m = 400$) of the enriched $\text{La}_2@C_{72}$ ($m = 1142$ Daltons) sample. Single photon ionization is performed with 157 nm radiation (7.90 eV) of a F_2 excimer laser, and the mass spectrum is therefore a true abundance spectrum. The most stable fullerenes C_{60} ($m = 720$ Daltons) and C_{70} ($m = 840$ Daltons) are also clearly visible.

the purification of selected metallo-fullerenes. In Figure 1 a mass spectrum (abundance spectrum) of a fullerene sample which contains about 5% $\text{La}_2\text{@C}_{72}$ is shown. The original sample contained approximately 0.05% of $\text{La}_2\text{@C}_{72}$ relative to C_{60} . This sample was enriched via HPLC-separation with a on π - π interaction based column. For further separation a column based on a different separation mechanism is needed. This separation/purification approach will only work for a restricted number of endohedral complexes, however. Some of the complexes will not dissolve in or even react with organic solvents whereas others will not be air-stable. If the guest atom or molecule is only weakly bonded (as with the encapsulation of closed shell systems) the endohedral complex will look identical to the corresponding empty fullerene from the outside, and chemical separation techniques are bound to fail. The current status of the endohedral fullerene research has recently been reviewed by Bethune et al.¹⁶

Apart from the chemically bonded internal fullerene complexes (like for instance La@C_{82}), species which are inert can be 'topographically' bound; an endohedral complex like He@C_{60} (though thermodynamically unstable at room-temperature) has a vanishingly low probability of decomposition because of the high activation barrier for the passage of the inert gas atom through the cage. Such metastable endohedral complexes formed via insertion reactions were first experimentally observed in molecular beam experiments under single collision conditions^{17,18}. Saunders et al.¹⁹ showed that He@C_{60} and Ne@C_{60} are being produced if the carbon arc-discharge is operated in a He or Ne atmosphere, respectively. In the latter case, volume arguments can be used to explain the abundance of the endohedral complexes relative to the empty ones (on the order of 10^{-6} under standard fullerene-production conditions). It should be noted that all commercially available fullerene samples will contain a comparable fraction of endohedral rare gas complexes, and these endohedral complexes can not be separated from the empty fullerenes by the standard analytical separation techniques.

It has recently been demonstrated that bulk quantities of metastable endohedral rare gas fullerene complexes can be formed by filling empty, chromatographically separated, fullerenes afterward. He, Ne, Ar, Kr and even Xe can be incorporated in C_{60} by pressurizing a fullerene sample up to 2500 atm with the inert gas at temperatures up to 620°C for a duration of a few hours. Typically a few tenths of a percent of the fullerene sample that survives these conditions is found to contain a single rare-gas atom, as determined via mass spectrometry²¹.

Recently, a spectacular ^3He NMR experiment has been performed on a sample containing a small fraction of endohedral $^3\text{He@C}_{60}$ and $^3\text{He@C}_{70}$ ²¹. The ^3He resonance of the endohedral He@C_{60} and He@C_{70} compounds are found down-shifted by 6.30 ± 0.15 ppm and 28.8 ± 0.2 ppm relative to the resonance of free ^3He atoms. Apart from the information this experiment yields on the interior of the fullerene cage, it is the first ^3He NMR spectrum of a 'stable' helium compound²¹.

Conclusions

Endohedral fullerenes can be treated as model systems for the study of properties of localized atoms, ions or molecules in a quasi-spherical potential and provide the unique possibility to tailor electronic, optical, vibrational and chemical properties on a molecular level. It has been demonstrated that species which would normally be considered inert can be 'topographically' bound and refrac-

tory materials can be put into the gas phase at much lower temperature. They can also be the basis of a new class of materials, with electronic and optical properties which can be tuned by placing various atoms, molecules or clusters inside the carbon cages of a fullerene crystal. Fullerenes containing a molecule with an electric dipole moment inside might be the building blocks for an ideal electric dipolar lattice, which would be a new form of ferroelectric materials. Given the fact that electrostatic interactions of C_{60} with extra-cavity metal atoms lead to phenomena like superconductivity, the yet unknown properties of fullerenes with atoms or molecules trapped inside form both a challenging and a promising research goal.

Up to now most information on the nature of the endohedral binding has been obtained by applying resonance techniques that are selectively sensitive to the internal guest, like EPR and NMR. These techniques can be, and have been, applied to diluted samples. To fully exploit this new research field, however, production of useful quantities of endohedral fullerenes with a sufficient purity is of crucial importance and this will be a real challenge for the experimentalists.

Acknowledgements

We would like to thank *P.H.M. van Loosdrecht* and *D.S. Bethune* at the IBM Research Center in Almaden CA. for the $\text{La}_2\text{@C}_{72}$ containing sample.

This work is financially supported by the 'Netherlands Organization for Scientific Research (NWO)', and is part of the research program of the 'Stichting voor Fundamenteel Onderzoek der Materie (FOM)'.

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