Nuclear recoil implosion for generating radioisotopically labeled fullerene endohedrals and cages

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The use of nuclear recoil for producing radioactive endohedral and cage-labeled fullerenes is presented, with special emphasis on the energy of chemical effects after nuclear particle capture. The different possibilities using (n,γ), (n,α), (p,n), (γ,α) and (γ,n) nuclear reactions are treated in detail.

Introduction

The worldwide interest in the discovery of fullerenes1 and their preparation in macroscopic amounts2 has led to a true epidemic growth3-5 of research in this field and has finally brought the chemistry Nobel Prize to KROTO, CURL and SMALLEY, in 1996. Along the multitude of interesting directions in fullerene research,6 one of the most promising one relates to the encapsulation of atoms into the inside of the fullerene cages by forming endohedral fullerenes.7,8

Both the properties, structure and dynamics of the atoms trapped in fullerene cavities have been intensively studied.6 Endohedrality was also approximated and described as a “guest-host” interaction.9-11 In a recent paper BRAUN argued that the formation of endohedral fullerenes seems to be more adequately described as a “capturer-captive” event.11

It has been emphasized that due to energetic considerations the building of endohedral fullerenes cannot be achieved by “conventional” chemical means,6 principally special synthesis procedures had to be elaborated based on the possible options.

(a) Atoms of X that are accidentally (or intentionally) present in the inner side of the all carbon clusters in the graphite plasma when the cluster closes are being captured by the fullerene cage. Assemblies formed in this way might be denoted as “capturands”.11

(b) Atoms of X can penetrate the shell of the fullerene cage in high-energy bimolecular collisions12 in the gas phase. A somewhat similar procedure involves colliding beams of thermal metastable atoms of He and Ne or fast ions with thin fullerene films14 with solid fullerene surfaces,12 resulting in their penetration into the fullerene molecules.

(c) Atoms of inert gases can penetrate the fullerene cage by a method which entails high pressure and heating the fullerenes to 650 °C with inert gases for 8 hours at a pressure of 3000 atm. in a copper ampoule.15

Procedure (a) simply requires that atom X being incorporated into the graphite rods prior the vaporization process during the arc vaporization method of KRÄTSCHMER and HUFFMAN.2 Mixtures of metal oxide, graphite powder and graphite cement are placed into holes drilled in graphite rods, and then heated from 200 to 1000 °C. It has been shown that the produced soot contains endohedral metallofullerenes as well as fullerenes.16-20

In what follows we describe a new option which can be used for building radioisotopically labeled endohedrals and of cage labeled fullerenes. The option comes from nuclear chemistry and we have been led to one aspect of it21 in a serendipitous way during our investigations on the trace element impurities in fullerenes and in fullerene precursors (e.g., graphite and graphite soot) by instrumental neutron activation analysis (INAA).22-24

Nuclear recoil

The procedure is based on the so called Szilárd-Chalmers effect which involves the chemical effects of fractions of energy released in nuclear transformations appearing as kinetic energy and causing atomic recoil and excitation. The repulsion energies of nuclear transformations lie in the range from about 1 eV to 1 MeV of kinetic energies. These chemical effects of nuclear transformations have been discovered by Szilárd and Chalmers in 1934.

A short time later Fermi pointed out that the recoil energy after a nuclear transformation, let say that of an atom emitting a prompt γ quantum following the neutron capture is sufficient to break chemical bonds. However, the same is valid for other nuclear processes, e.g., (n,α), (n,p), (p,n), (γ,α) and similar reactions and the recoil energy cannot only break but build chemical entities.
The recoil energy of a target atom after a nuclear reaction is obtained from the following expression,

\[ E_R = \sum I_q E_{\gamma q}^2 / D_c M \sum I_q \]

where \( E_R \) means the weighted mean value of the recoil energy in eV, \( M \) the atomic mass of the product nucleus and \( E_{\gamma} \), the energy of the prompt \( \gamma \)-quantum in MeV emitted with \( I_q \) intensity. The symbol \( D_c \) represents a dimensional constant. For atoms with masses of between 20 and 200 the recoil energy would vary between about 1000 eV and 100 eV, assuming a single prompt \( \gamma \)-ray emission of 6 MeV. This is higher than that of most of the chemical bonds, which usually have energies of some eV (e.g., the average energy for a C-C bond rupture is of about 9-10 eV in fullerenes).

The recoil atoms resulting from a nuclear reaction run a certain distance before being thermalized. They lose their energies upon excitation, ionization and elastic collisions with atoms of the medium. After a reduction of the recoiled atoms' kinetic energy to below of approx. 100 eV, chemical interactions can occur through the mediation of these collisions, whereby the kinetic energy of the nuclide is still very high in comparison with the thermal motion energy of the molecules.

**Recoil effects in fullerene cages**

*Endohedral atom implosion by nuclear recoil via \((n, \gamma)\) reactions*

During their investigations of trace element impurities in fullerenes \(22,23\) BRAUN and RAUSCH \(21,22\) studied neutron activation of solid \(C_60\) which contained relatively high impurity levels (approx. 200 ppm) of argon. After neutron irradiation of the samples in a nuclear reactor they have found residual radioactivity of \(^{41}\)Ar in the toluene solutions of irradiated \(C_60\) in spite of their considerable effort to expel any residual free \(^{41}\)Ar gas. They attributed their results to the endohedral argon compound \(^{41}\)Ar@\(C_{60}\) formed by prompt gamma recoil of the \(^{41}\)Ar target nuclide in the \(^{40}\)Ar(\(n, \gamma\))\(^{41}\)Ar nuclear reaction.

Recent investigations by GADD et al. \(24,25\) on stoichiometric rare gas interstitial fullerenes (e.g., \(Ar_1C_{60}\)) produced by isotopic pressing of solid \(C_60\) in the presence of Ar, Kr or Xe and irradiated with neutrons in a nuclear reactor estimated that 1-2% of the activated rare gas atoms, which recoil as a result of prompt gamma-ray emission, end up endohedrally in what is most likely to be the \(C_{60}\) molecule or some other fullerene derivative. On this basis they demonstrated the formation of \(RN@C_{60}\) where \(RN\) stands for a radionuclide of \(^{125}\)Xe, \(^{133}\)Xe, \(^{41}\)Ar or \(^{85}\)Kr.

In both of the abovementioned endohedral implosions by nuclear recoil there was no noticeable radiation damage to the \(C_{60}\) molecule itself. Namely the gamma-rays emitted caused no bond breaking and earlier investigations by BRAUN et al. \(27\) have shown that reactor neutron irradiation in a thermalized position (\(\Theta > 50\) or above) does not affect the structure of \(C_{60}\) up to a total thermal neutron dose of about \(10^{16}\) n cm\(^{-2}\) s\(^{-1}\).

Recent investigations by BRAUN and RAUSCH have shown that the use of \((n, \gamma)\) nuclear reactions for the implosion of recoiled atoms into fullerene cages can be considered as a general procedure for producing many endohedral compounds. \(28\)

*Endohedral atom implosion by nuclear recoil via \((n, \alpha)\) reactions*

JIMÉNEZ et al. \(29\) have used the Szilárd-Chalmers effect to incorporate tritium atoms into \(C_{60}\) molecules. The incorporated tritium was generated in a nuclear reactor via the \(^{6}\)Li(\(n, \alpha\))\(^{3}\)T nuclear reaction. The generated hot tritium atoms slowed down and ended up inside the \(C_{60}\) cage where they remained trapped.

JIMÉNEZ et al. synthesized a lithium salt of the \(C_{60}\) (e.g., \(Li_6C_{60}\)) to ensure intimate contact between the lithium atoms and the \(C_{60}\) molecules before the neutron irradiation. They irradiated the \(Li_6C_{60}\) samples in a nuclear reactor for 30 s at a neutron flux of \(1.5 \times 10^{13}\) n cm\(^{-2}\) s\(^{-1}\). After irradiation some tritium has been shown to be in fact endohedrally incorporated into \(C_{60}\) but contrary to the previously mentioned \((n, \gamma)\) reactions they also noticed a large radiation damage of \(C_{60}\) being transformed into an insoluble tar which was presumed to have been irradiation generated. The radiation damage observed by JIMÉNEZ et al. at a thermal neutron dose of about \(10^{13}\) n cm\(^{-2}\) seems to be less due to the bombarding neutrons but to the emitted alpha particles whose mass, energy and range, when close to the \(C_{60}\) molecule, is large enough to do serious damage and to destroy the fullerene molecule.

A far more efficient way to incorporate tritium atoms into \(C_{60}\) via recoil implantation based on the \(^{6}\)Li(\(n, \alpha\))\(^{3}\)T nuclear reaction \(30\) would be the use, instead of synthesized \(Li_6C_{60}\) target crystals, a mixture of polycrystalline \(Li_2CO_3\) and \(C_{60}\) particles of 30-40 \(\mu\)m diameter intimately mixed and homogenized in a 4-8% slurry and then irradiated with thermal neutrons. Namely in this case the \((n, \alpha)\) reaction would occur within the \(Li_2CO_3\) crystals. The range of the produced \(^3\)T nuclide is about 50 \(\mu\)m, so the tritium would escape the \(Li_2CO_3\) particles to act as recoiling atoms whose energy is sufficient to implode into the \(C_{60}\) cage. The range of the bulky alpha particles being less than that of the tritons (e.g., about 10 \(\mu\)m), they could not be able to escape the \(Li_2CO_3\) crystals and would not produce indiscriminate damage to the \(C_{60}\) nearby molecule.