Beam Implantation: A New Method for Preparing Cage Molecules Containing Atoms at High Incorporation Levels

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Getting atoms inside cage molecules such as fullerenes is of considerable theoretical and practical interest.[1] The methods used to do this include forming the cage in the presence of the species to be included[2,3] and also their introduction into the preformed cages through "windows" which can be temporarily opened.[4] Both methods are limited in the incorporation level (fraction of the cages which are occupied in the product) achievable because of thermodynamic considerations. One cannot get to incorporation levels beyond the relatively low amounts mandated by the in−out equilibrium constants.[5] Due to kinetic problems, the fullerenes containing noble gas atoms which we have produced, so far, contain far less than the equilibrium incorporation levels.

We describe here a new method for preparing cage molecules containing atoms which, in principle, is not limited to thermodynamic levels of incorporation. Beams of ions can be easily made at selected energies. On colliding with cage molecules, they have a chance of penetrating into the interior. If one exposes the molecules to the beam particles continually and if these collisions neither knock occupants out of the cages nor destroy occupied cage molecules, there is no upper limit to the fraction of occupation which can be achieved.

It has already been shown[6] that collisions between C_{60} and helium and neon cations and/or C_{60}^+ and the neutral noble gas atoms in the gas phase lead to the production of fullerene ions containing the noble gas. However, the number of ions is so small that neutralizing them and accumulating the product molecules in sufficient amount for further study would be difficult or impossible. Therefore, this is not a practical route to prepare these materials.

We have found that impinging beams of He^+ or Ne^+, generated in a vacuum chamber, onto freshly deposited solid C_{60} surfaces results in incorporation of the noble gas inside the fullerene. Milligram quantities of material are deposited in each run. The product is dissolved in CS_2. The amount of noble gas incorporated is measured using our standard procedure, through releasing it at 1000 °C for analysis by mass spec-

Table 1

gas	ion energy (eV)	total incorporation[a]	efficiency[b]	incorporation fraction[c]
He	30	3.9×10^{-11}	1.2×10^{-4}	3×10^{-5}
He	60	6.2×10^{-10}	4.4×10^{-4}	4.5×10^{-4}
He	100	3.0×10^{-10}	2.2×10^{-4}	2.1×10^{-4}
He	130	2.7×10^{-10}	4.5×10^{-4}	1.9×10^{-4}
He	230	1.4×10^{-10}	1.8×10^{-4}	1×10^{-4}
Ne	130	background		
Ne	230	5.1×10^{-11}	1.1×10^{-4}	4×10^{-5}

[a] Total number of moles of noble gas in the sample. [b] Calculated from *a*/(moles of ions hitting the target). [c] Calculated from (moles of noble gas)/(moles of fullerene).
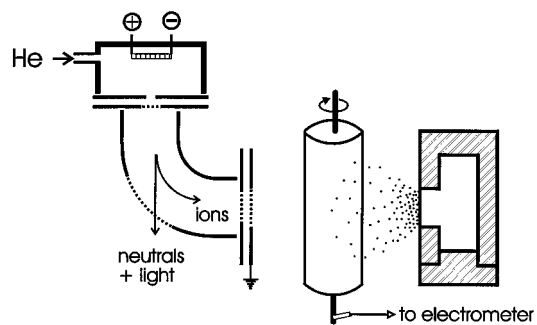

Figure 1. The element on the right is the fullerene effusive source. The rotating target is in the center.

troscopy.[7−9] Even though our new process occurs in a vacuum, the incorporation levels are comparable to those obtained in our standard thermal method at 3000 atm at 650 °C.[4] We expect that increasing the beam current or decreasing the rate of deposition of the fullerene will enable us to increase the incorporation level considerably. If we do this with ^3He, we will be able to extend the, already powerful, helium NMR method for following fullerene chemistry.[2] Samples with high incorporation levels should make it possible to obtain the IR and UV spectra of the occupied fullerenes. It is likely that we can ultimately put more than one noble gas atom into a fullerene.

The probability of penetrating the cage is a function of the ion energy (Table 1). Satisfactory incorporation occurs over a range of energies. Only at ion energies above 100 eV for helium and somewhat higher energies for neon does there appear to be any damage to the fullerene. Fullerene damaged in this way is insoluble in CS_2. In the solid after collisional impact, C_{60} molecules can efficiently transfer excess internal energy to neighboring fullerenes rather than fragment.

The apparatus is shown schematically in Figure 1. The fullerene beam emerges from an oven heated to 470 °C and deposits on a rotating aluminum cylinder. The other side of the cylinder is exposed to ions generated by a DC discharge in the noble gas and accelerated to the desired energy. The ions are deflected 90° by a pair of plates before collision in order to separate them from neutral particles and UV light produced in the source. The charge is neutralized through conduction to the cylinder allowing convenient measurement of the current ($\sim$5 μA). By rotating the whole source assembly by 90°, we can expose the fullerene surface to the neutral component of the beam, while excluding ions. Under these conditions, we also see incorporation of both helium and neon, and we believe that reaction with thermal, metastable helium and neon atoms

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is responsible for this result. We do not know the mechanism of this process.

Gas phase ion collision studies[6] indicate that heavier noble gas atoms will be more difficult to incorporate this way. However, separation methods[7,8] can be used to enrich fullerenes labeled with our high-pressure method to achieve high incorporation levels of these atoms.

After this manuscript was submitted, Tellgmann et al. published a report[10] describing a basically similar procedure for exposing C_{60} to beams of Li^+, Na^+, K^+, and Rb^+ ions. The material obtained was analyzed by laser-desorption mass spectroscopy, and $C_{60}M^+$ ions were detected. Whether the metal atoms penetrate the fullerene cage or not, they would be deposited together with the fullerene and would likely form the

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well-known external fullerene salts. Exposure of such salts to a laser beam could well produce the ions observed. While it is likely that some energetic metal ions could penetrate the fullerene cage, the results reported do not provide credible evidence that this has occurred in the experiments described. In contrast with the noble gas work described above, no extraction of the material formed into a solvent for characterization was reported.

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