Journal of
Computational and Theoretical Nanoscience
Vol. 5, 1–8, 2008

Molecular Dynamics Simulations of Noble Gas Release from Endohedral Fullerene Aggregates Due to Cage Disintegration

M. K. Balasubramanya[1,*], M. W. Roth[2], P. D. Tilton[1], and B. A. Suchy[2]

[1] Department of Physical and Environmental Sciences, Texas A&M University-Corpus Christi, 6300 Ocean Drive, Corpus Christi, Texas 78412, USA
[2] Department of Physics, University of Northern Iowa, Cedar Falls, Iowa 50614, USA

We report the results of molecular dynamics simulations of the release of five species of noble gas atoms trapped inside a small aggregate of fullerenes in the temperature range 4000 K $\leq T \leq$ 5000 K. We find that larger noble gas atoms are generally released at a slower rate and that helium is released considerably more rapidly than any of the other noble gases. The differing release rates are due not only to the differences in the size and mass of a given endohedral species but also because larger trapped atoms tend to stabilize the fullerene cage against thermal fluctuations. Unlike the case of atoms entering fullerenes, we find that any atom escaping from the cage results in a window which does not close. Escape rate constants are reported and comparisons with experiment are discussed.

Keywords: Fullerene, Endofullerene, Fullerite, Aggregate, Molecular Dynamics.

RESEARCH ARTICLE

1. INTRODUCTION

Endohedral fullerenes, or carbon cages trapping atomic or molecular species, have received significant attention both experimentally[1–16] and theoretically.[17–33] Such systems with noble gas atoms trapped inside the molecular cage are formed while making fullerenes by passing an electric arc between carbon electrodes in an inert atmosphere of noble gases. Much interest has focused on the behavior of these systems for primarily two reasons. Endofullerenes are found terrestrially at meteor sites with ^{3}He trapped inside. Their study can throw light on their extraterrestrial origins, especially the prevalent conditions at the time of their formation.[34] Secondly, chemists have been interested in encapsulating noble gas atoms inside fullerene cages and study the interactions between the host and guest. Cross and Saunders[35] have pioneered the insertion of ^{3}He into C_{60}. This endohedral molecule is chemically modified outside the cage in different ways and subjected to NMR analysis. Since every ^{3}He-labeled fullerene has a distinctive helium chemical shift, that shift can be used to pin down the structure of the derivative, as well as monitor the molecule's subsequent chemical transformations. ^{3}He NMR spectroscopy has thus become one of the most powerful tools for following fullerene chemistry. In addition to He, four other noble gases—Ne, Ar, Kr and Xe—have been inserted into fullerenes, making unusual and highly stable noble gas compounds in which no formal bond exists between the noble gas and the surrounding carbon atoms.

A very convenient way to experimentally probe an endohedral fullerene system is to raise its temperature until the encapsulated species is released, and to subsequently measure the concentration of the released species. Measurements have been made[15] of the release of Ne from endohedral Ne@C_{60}. It is possible for the fullerene to release a Ne atom without the fullerene structure being destroyed, which is impossible if the Ne atom is simply pushed through the molecular cage, breaking the C—C bonds. Moreover, in the presence of impurities, the rate of release of trapped noble gas atoms is increased by orders of magnitude. A modified windowing mechanism has therefore been proposed, where the impurity (e.g., radical) adds to the cage and weakens fullerene bonds. The endohedral atom, according to this model, exits from the 'weak spot' of the cage, or its 'window,' followed by the impurity detaching from the carbon atoms cage, thus allowing reconstitution of the C—C bonds and the fullerene cage.[15] We conducted molecular dynamics (MD)

*Author to whom correspondence should be addressed.