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Simulated dynamics of Ne@C_{60} aggregates beyond dissociation

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Molecular dynamics (MD) computer simulations are utilized to better understand the dynamics of small ($N = 5$) endohedral Ne@C_{60} aggregates. Multiple runs at various temperatures are used to increase the reliability of our statistics. The aggregate holds together until somewhere between $T = 1150$ and 1200 K, where it dissociates, showing no intermediate sign of melting or fullerene disintegration. When the temperature is increased to around $T = 4000$ K, the encapsulated neon atoms begin to leave the aggregate, with the fullerene molecules still remaining intact. At temperatures near $T = 4400$ K, thermal disintegration of the fullerenes preempts the aggregate dissociation. Above this temperature neon atoms are more quickly released and the fullerenes form a larger connected structure, with bonding taking place in atom pairs from different original fullerene molecules. Escape constants and half lives are calculated for the temperature range $4000\,\text{K} \leq T \leq 5000\,\text{K}$. The agreements and disagreements of results of this work with experiments suggest that classical MD simulations are useful in describing fullerene systems at low temperatures and near disintegration, but require development of new techniques before it is possible to accurately model windowing at temperatures below $T = 3000$ K.

Keywords: Endohedral fullerenes; Molecular dynamics; Noble gases; Encapsulation

1. Introduction

For two decades, fullerenes have remained at the forefront of scientific curiosity and research efforts. They are physically interesting molecules in their own right and can display a rich diversity of behavior when they have atoms trapped inside their cages or have other atomic and molecular species adsorbed on their exterior. Because of their symmetry and durability it is of interest to place various atoms within a fullerene cage and study the dynamics of this endohedral system. Many experimental [1–14] and computational [15–28] studies address the behavior of endohedral fullerene/noble gas systems as well as the dynamics of fullerene systems and how they may encapsulate certain atoms. Encapsulation of noble gases by fullerenes happens frequently during the molecules' formation in the presence of noble gases at extraterrestrial sites and in the laboratory production processes employing an electric arc between carbon electrodes in a noble gas environment. Specifically, helium isotopes may be trapped in fullerenes found in extraterrestrial objects or even on the ancient earth and, if the sample size is large enough, unique helium isotope ratios are preserved and can, therefore, be calculated [29]. Study of such helium isotope ratios in endohedral fullerenes yields significant information about the extraterrestrial microscopic environment at the time of their formation.

Another interesting aspect of encapsulation is that for an aggregate of fullerene/endohedral noble gas molecules, the release of the encapsulated species can be studied as functions of temperature and time. Shimshi *et al.* [30] completed a mass spectroscopic study of the release of Ne@C_{60}. They found that it was possible for the fullerene to release a Ne atom without the molecular cage being destroyed, which is impossible if the Ne atom is simply pushed through the cage. Therefore, they attribute the release of the encapsulated species to a window mechanism [15,16]. Such a mechanism involves temporary carbon–carbon bond breaking which disrupts the hexagonal/pentagonal bond symmetry, opening the cage up for guest atom escape. After a guest atom has passed through the opening, the bond will re-form. They also find that, in the presence of impurities, the rate of release is increased by orders of magnitude. The half life for Ne escape at $T = 903$ K is more than one month but at $T = 1173$ K it is on the order of 10 h. Here, a modified window mechanism has been proposed, where the

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