Chapter 15

Graphene and Fullerenene Clusters: Molecular Polarizability and Ion–Di/Graphene Associations

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ABSTRACT

Interacting induced-dipoles polarization in code POLAR permits calculating molecular polarizability, which is tested with endohedral metallofullerenes Sc\(_n\)@C\(_m\) and clusters C\(_n\) (fullerene, graphene, GR). Polarizability identifies aggregates with dissimilar numbers of atoms and separates isomers. Results are of the same order of magnitude as reference computations performed with code PAPID. Polarizability bulk limit is estimated from Clausius–Mossotti relationship. Polarizability trend for clusters vs. size is unexpected: they are more polarizable than bulk. Theory yielded the same for small Si\(_n\), Ge\(_n\), and GaAs\(_n\); however, experiment oppositely deferred for larger Si\(_n\), GaAs\(_n\), and GeTe\(_n\). Smaller clusters do not behave like intermediate sizes: polarizability of small aggregates is caused by dangling bonds at the surface that resembles metallic. Varying number of atoms, clusters show peaks indicative of particularly polarizable structures in agreement with alkalines polarizability and molar volume in the periodic table of the elements. Code AMYR calculates molecular associations on GR\(_{2j}\)–M\(^{+}\).

INTRODUCTION

Research opportunities in studying the role of size in modifying the properties of a material were exploited (Alford et al., 1990; Andres et al., 1989; Bloomfield et al., 1985; Jarrold, 1991). In one example, clusters were deposited on an inert substrate and probed with photons (Honea et al., 1993). In another one, a cluster beam was produced (Cheshnovsky et al., 1987). Based on interatomic potentials, the structure

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of Si_{13} is special (Chelikowsky et al., 1991). The predicted ground state is a close-packed icosahedron. Unfortunately, studies based on ab initio methods yielded a structure, which is a capped antiprism structure (Grossman & Mitás, 1995). It was proposed that current electronic structure theory is not capable of handling exchange and correlation contributions in this system (Phillips, 1993). Nanocrystalline powders were used to synthesize materials with physical processing, e.g., sintering (Brus, 1986; Kayanuma, 1988). Rutile processing reduced sintering temperatures by hundreds of degrees without sacrificing desirable mechanical properties (Siegel, et al., 1988). Quantum confinement was used to engineer excitation energy (Alivisatos, 1996). Computations predicted that crystallized C_{60} fullerite is a direct band-gap semiconductor like GaAs (Benning et al., 1991; Jost et al., 1991; Martins et al., 1991). Benichou et al. (1999) measured Li_n (2 \leq n \leq 22) polarizability. Maroulis and Xenides (1999) reported ab initio calculations for Li_n. Fuentealba (1998) presented a density functional theory (DFT) study of the polarizability of C_n (n \leq 8). Fuentealba & Reyes (1999) computed the polarizability of Li_nH_m via DFT. Jackson et al. (1999) used a DFT-based method to calculate Si_n (10 \leq n \leq 20) polarizability. Deng et al. (2000ab) computed Si_n (9 \leq n \leq 28) polarizability via a DFT cluster method. Hohm et al. (1998) deduced As_n experimental polarizability from the analysis of refractivity measurements in As vapour.

The notion that atoms could be trapped in fullerene cages (Kroto et al., 1985) was supported by mass spectral evidence that La–fullerene complexes were produced by laser vaporization of La-impregnated C_{graphite} (Bethune et al., 1993; Heath et al., 1985). Techniques to produce metallofullerenes in bulk were developed allowing detailed spectroscopic characterization of a metallofullerene and leading to experimental studies of endohedral fullerenes (Chai et al., 1991; Johnson et al., 1992). By analogy with alkali-doped fullerenes in which electrons are donated to the fullerene cage by interstitial metal atoms, solid-metallofullerenes conductivity will depend on the internal dopant (Haddon et al., 1991); some may be superconductors (Hebard et al., 1991). Endohedral fullerenes containing small polar molecules could be assembled into ferroelectric materials (Cioslowski et al., 1991; Cioslowski & Nanayakkara, 1992). The production of fullerenes containing internal species complements the work on fullerene chemistry involving reagents outside the carbon cage (Taylor & Walton, 1993). Several mono-metallofullerenes M@C_n (Park et al., 1993), di-metal M_2@C_n (Suzuki et al., 1995) and a few tri-metal species, e.g., Sc_3@C_n were characterized (Beyers et al., 1994). A few noble gas elements were trapped inside the fullerene cage, which made the observation of unusual physical and chemical properties of isolated atoms encircled by a π-electron cloud possible (Saunders et al., 1993, 1994). Spectroscopic techniques showed that the charge is transferred from the encapsulated metal atoms to the fullerene surface. These atoms will form clusters with weak metal–metal bonds. The clusters also donate electrons to the cage (Breton et al., 1993). C_{graphene} (GR) atoms exhibit sp^3 hybridization which, together with atomic thickness, makes it unique. The C–GR and nanotubes (CNTs) show strong third-order nonlinearity. The electronic properties of GR semiconductor monolayers are better than those of bulk spawning efforts to create functionalized monolayers of other bonded crystals. Higher carrier mobility is achieved via ultra-thin topologies but terminating monolayers with ligands for specific applications, ultra-thin materials are made far more sensitive than bulk for sensors. Solvent selection was analyzed (Hernandez et al., 2008; Khan et al., 2010; Zhang et al., 2010). The GR-like layered materials were produced (e.g., WS_2, MoS_2, BC_2N, BC_3, BN). In this laboratory Bosch-Navarro et al. (2012, 2013ab) examined multifunctional hybrid nanocomposites based on CNTs and chemically modified GR.

In earlier publications, Sc, C_{fullerene} (Torrens, 2000a), Sc–hexagonal close packing (HCP), GR (Torrens, 2001, 2002ab), Si, Ge, GaAs (Torrens, 2002c, 2004a) clusters and GR_{(i)}–cation interactions (Torrens & Castellano, 2013) were calculated with our code POLAR and our version of code atomic polarizabilities.