Low Hydroxylated Fullerenes: Stability, Thermal Behavior, and Vibrational Properties

M. V. Velarde-Salcedo[a], M. Gallo[b], and R. A. Guirado-Lopez[c]

[a]Universidad Autónoma del Estado de México, Instituto Literario 100, CP 50000, Toluca

[b]Tecnologico Nacional de Mexico/ITCJ, Av. Tecnologico 1340, Cd. Juarez, Chihuahua 32500, Mexico

[c]Instituto de Física “Manuel Sandoval Vallarta”, Universidad Autonoma de San Luis Potosí, Alvaro Obregon 64, San Luis Potosí, S.L.P. 78000, Mexico

Extensive density functional theory calculations dedicated to analyze the stability, thermal behavior, as well as the infrared and Raman spectra of low hydroxylated fullerenols C60(OH)12 are presented. It is found that the formation of local networks of hydrogenbonded OH groups plays a fundamental role in the stability of these complexes. The calculated dipole moments, polarizability values, optical gap, and Fukui functions of C60(OH)12 isomers strongly depend on the structure of the hydroxyl overlayer, thus being an important parameter to tune the material properties. DFT Born−Oppenheimer molecular dynamics calculations at T = 300 K reveal that aggregated forms of OH groups on the fullerene surface show an interesting dynamical behavior, characterized by a continuous proton-exchange process between neighboring hydroxyl molecules that modifies the structure and chemical nature of the molecular coating. From nudged elastic band studies analyzing OH diffusion on the C60 surface, energy barriers opposing OH migration of ∼1 eV are found. However, in the presence of surrounding H2O species, a water-assisted diffusion process is obtained which can reduce the energy barriers to values as low as 0.25 eV. The comparison between experimental and calculated IR spectra of various C60(OH)12 isomers shows well-defined spectral features which can be helpful to identify the structure of these fullerene complexes. Finally, simulations of the wavelength-dependent Raman spectra of hydroxylated fullerenes reveals (i) that the intensities of the Raman active modes strongly depend on the excitation laser and (ii) the importance of the wavelength-dependent calculations to reveal precise features of different regions of the spectra (J. Phys. Chem. C 2018, 122, 13117−13129).