Inner-shell electronics of caged molecules: small molecules in carbon cages

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Molecular electronics is the subject of intriguing changes taking place when a molecule happens to be confined in a cage. What kind of changes are they? Answering the question we are approaching to understanding of many elementary processes that occur in complex composite systems.

Special emphasis is put here on unoccupied valence states of a quasifree molecule that is confined in a nanosize carbon cage. X-ray absorption and inner-shell photoionization spectra are regarded as a basic probe of the cage effects. Their origin is being attributed mainly to (i) changes in molecular dynamics [1], (ii) electron scattering at the cage [2] and (iii) dynamic polarizability of the cage [3]. These phenomena are discussed.

Inner-shell electronics of caged molecules is examined in small molecular species (CO, N_2, SF_6) confined in fullerenes, carbon onions and nanotubes, and nanoporous carbon. Two limiting cases of weak and strong cage effects are revealed and described. To describe and compute the X-ray absorption and inner-shell ionization spectra the quasiatomic approach is applied. We have revealed the *red-* and *blue-shifts* of core-to-valence excitations and new resonance states in spectral distribution of oscillator strength for continuum transitions in the caged molecules and in the cages. These new states demonstrate different nature and can be attributed to either *confinement* resonances or *window-like* resonances or *induced shape* resonances. It is shown that the red- and blue-shifts correspond to the weak cage effect whereas the new resonances appear as a consequence of the strong effect. The experimental evidences of the cage effects are presented and the specific conditions of their observation are determined.

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