Long-Range Electron Effects upon Irradiation of Molecular Solids and Polymers

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Long-range electron effects are responsible for specific localization and selectivity of the radiation-induced chemical transformations occurring in molecular solids and polymers, when the classic diffusion mobility is essentially restricted. In particullar, understanding of the effects of this kind may be of key significance for establishing new ways to control the radiation sensitivity of macromolecules and organized polymeric systems, nanomaterials and biopolymers. This talk will present an overview of model studies of the long-range electron effects with the characteristic scale from several angstroms to ten nanometers.

The following aspects of the problem will be analyzed:
(1) Positive hole delocalization in ionized molecules. This phenomenon has been demonstrated experimentally and confirmed by quantum chemical calculations for a number of various-type molecules (alkanes, conjugated polyenes, bifunctional compounds). The effective delocalization length was found to be up to 2 nm (or even larger). The role of this effect in site-selective radiation chemistry will be discussed in the frame of concepts of distributed reactivity and "switching" between delocalized and localized states.

(2) Trap-to-trap positive hole and electron migration between isolated molecules or functional groups. The characteristic distance for this process was estimated to be 2 to 4 nm. Special impact will be made on the possible role of this process in selection of specific isomers or conformers upon irradiation of complex systems and macromolecules.

(3) The effects of long-range scavenging of low-energy secondary electrons in polymers and organized polymeric systems. As revealed by model experiments, the radius of electron capture in solid polymers may be in the range of 1 to 10 nm. Possible implications of scavenging effects for controlling the radiation chemistry of polymers and organized polymeric systems will be considered.

This work was supported in part by the Russian Foundation for Basic Research (project no. 06-03-33104.