

Accommodation of Electronic Excitation in sigma-Bond Systems: Peralkylated Oligosilanes

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The geometrical relaxation that follows the first singlet excitation of a sigma-electron system, such as a saturated hydrocarbon or its silicon analog, an oligosilane, is likely to be more deep-seated than an analogous relaxation of a pi-electron system, because in the former case one of the very electrons that form the only bonds that hold the molecule together is being promoted to an antibonding orbital. Many though not all of these sigma electron systems fluoresce, especially at low temperatures. The Stokes shifts are often but not always extremely large, 2 - 3 eV, leaving no doubt that in many cases the relaxed excited state geometries differ very significantly from the equilibrium geometries of the ground state. We have chosen a series of peralkylated oligosilanes and asked (i) how molecular structure (linear, cyclic, or branched), size, and conformation determine the magnitude of the Stokes shift, (ii) what are the relaxed geometries in the lowest excited singlet state S_1 , and (iii) what is the degree of excitation delocalization in the relaxed S_1 state. We have addressed these questions using several ab initio procedures and empirical as well as ab initio density functional methods and the results will be reported and discussed. Some of the salient results are (i) the degree of excitation delocalization is determined by conformation of the longest linear chain and is closely tied with the magnitude of the Stokes shift, (ii) unlike the ground state equilibrium geometries, in which all silicon atoms are tetrahedral, the localized S_1 geometries tend to contain one silicon atom at a trigonal bipyramidal geometry, or two adjacent silicon atoms at a geometry intermediate between tetrahedral and trigonal bipyramidal, (iii) four of the vertices in the trigonal bipyramid are occupied by the same substituents that were present in the ground state and the fifth vertex is occupied by an odd-electron-carrying hybrid orbital of intermediate valence/Rydberg nature, composed primarily of silicon $4s$ and $4p$ atomic orbitals, with an admixture of $3d$. A similar observation of five stereoactive "valence" orbitals on a silicon atom was made for certain conformations of the radical anion of peralkylated tetrasilane and we propose that electron traps in amorphous silicon, responsible for the Staebler-Wronski effect that plagues its use in solar cells, have a similar trigonal bipyramidal structure.