

Singlet and triplet transitions in the optical UV absorption spectrum of perylene

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Abstract

UV-Vis optical absorption spectra were obtained for perylene in different solvents. The survey UV-spectrum of singlet transitions in cyclohexane and UV-spectrum of triplet transitions in bromopropane were recorded. The method of registration of triplet transitions was employed, based on the use of a cell with a large optical path length and bromo-substituted solvent. The presence of a heavy Br atom increases the spin-orbit interaction in the investigated molecule and thus the probability of excitation to triplet states. Assignment of the singlet and triplet electronic excited states and their attribution to the specific dominating electronic configurations were carried out using TD DFT B3LYP/6-31G quantum chemical calculations. The specific features of the occupied and vacant molecular orbitals involved into electron transitions were characterized via consideration of the photoelectronic spectra of perylene, found in the literature, and assigning the observed photoionization bands to the calculated B3LYP/6-31G orbitals. The energy of the first (lowest) vertical triplet transition was shown to be 1.92 eV, lying by ca. 0.4 eV higher than corresponding adiabatic transition known from the luminescence measurements made by other authors.