On the Estimation of Excited-State Dipole Moments from Solvatochromic Shifts of Absorption and Fluorescence Spectra

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The effect of the solvent polarity parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ appearing in solvatochromic theories, and the effect of the molecular shape of the Onsager cavity (sphere, ellipsoid of revolution) on the determined electric dipole moments μ_e in the singlet excited state are studied. It is found that the shape of the solute does not exhibit a significant effect on the determined values of μ_e, but only on the solvent parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ as well as on the Onsager radius a. Passing from a sphere to an ellipsoid leads to such a change in the scale that induces a proportional change in the slope coefficients m_1 and m_2. Also the effect of α/a^3 (α and a are the mean isotropic polarizability of the solute and the Onsager cavity radius in a homogeneous dielectric, respectively) on the determined values of μ_e has been studied, and it is found that the assumption $\alpha/a^3 = 1/2$ is valid in many cases.

Key words: Solvatochromic Absorption and Fluorescence Band Shifts; Dipole Moments in the Ground and Excited States; Shape of the Onsager Cavity.