Non-linear optical susceptibility and local-field factors in liquid chloroform: A time-dependent density-functional theory study

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Organic molecules are promising candidates for new non-linear optical materials and devices, potentially cheaper and higher performance than inorganic crystals. Design and initial characterization are typically done from the standpoint of isolated molecules, but when the molecules are put into solution or other condensed phases for measurement or application, the nonlinear optical properties are modified by the effect of the environment, making comparisons with the isolated molecule difficult in theory or experiment. To probe these environmental effects, we employ a new theoretical approach for direct calculation of the nonlinear susceptibility for the electric-field-induced second-harmonic generation (EFISH) and hyper-Rayleigh scattering (HRS) experiments in solution, based on molecular dynamics and time-dependent density-functional theory (TDDFT) with the Sternheimer equation. Additionally we show a rigorous definition of local-field factors usable for ab initio calculations, which can differ significantly from those obtained from the simple models typically used. These analyses allow us to make a direct comparison to measurements in condensed phases and to extract molecular properties.