

# The Nano-Engineering of Extraordinary Electro-Optic Materials Exploiting Guidance From First-Principles Theory

Larry R. Dalton

*University of Washington, Bagley Hall 202, Seattle WA 98195-1700*

Realization of large electro-optic (EO) activity for dipolar organic chromophore-containing materials requires the simultaneous optimization of chromophore first hyperpolarizability ( $\beta$ ), acentric order ( $\langle \cos^3\theta \rangle$ ), and number density (N). As these parameters are inter-related, correlated quantum and statistical mechanical calculations are required to understand the dependence of macroscopic EO activity upon chromophore structure and intermolecular electrostatic interactions. Correlated real-time, time-dependent density functional theory (RTTD-DFT) and pseudo atomistic Monte Carlo (PAMC) calculations are used to understand the dependence of linear and nonlinear optical properties on dielectric permittivity, optical frequency, and a variety of specific spatially-anisotropic interaction that can be nano-engineered into the macroscopic material structure. Structure/function relationships are considered for three classes of organic EO materials: (1) Chromophore/polymer composite materials; (2) chromophore covalently incorporated into passive (non-chromophore-containing) hosts; and (3) chromophores incorporated into chromophore-containing host materials—a new class of materials referred to as binary chromophore organic glasses (BCOGs).

To check the utility of correlated RTTD-DFT and PAMC calculations, macroscopic electro-optic tensor elements were measured by attenuated total reflection (ATR) and orientationally-averaged  $\beta$  values were measured by femtosecond, wavelength-agile Hyper-Rayleigh Scattering (HRS) in solutions of different dielectric permittivities. Dielectric constants were also measured and a new technique for measuring poling-induced order of chromophores was introduced based on variable angle polarized absorption spectroscopy utilizing light of both “s” and “p” polarizations. This new technique permits measurement of the even order parameter,  $\langle P_2 \rangle$ . Theoretical methods were used to compute each of these experimental parameters. Excellent agreement is observed between theory and experiment for all three classes of EO materials. Theory also suggested that acentric order could be improved by executing laser-assisted electric field poling (LAEFP) experiments on high  $\beta$  chromophores incorporated into the DR1-co-PMMA host polymer (Aldrich Chemical). Such LAEFP experiments result in factors of 2-3 improvement in EO activity as a function of irradiation of the charge transfer transition of the DR-1 chromophore with linearly or circularly polarized light. Theory-guided design of new organic EO materials has resulted, since 2000, in improvement of EO activity at a rate exceeding Moore’s Law to current values on the order of 500-600 pm/V. Improved EO values have led to devices exhibiting drive voltages of 0.25 V.

The correlation of theoretical and experimental data in the study of EO chromophore-containing materials provides major new insight into intermolecular electrostatic interactions and into the effectiveness of various theoretical methods in treating complex systems including polymers, dendrimers, and liquid crystalline materials. Insights gained are also relevant to the understanding of organic electronic, photovoltaic, light emitting, and photorefractive materials as well as nonlinear optical materials.

Email: dalton@chem.washington.edu