

Effective molecular polarizabilities and crystal refractive indices from wavefunctions constrained to fit X-ray structure factors

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We are undertaking detailed charge density studies on a series of organic molecular crystals with known nonlinear optical (NLO) susceptibilities. In general, the crystallography of important NLO materials is not well described, and although some have been the subject of charge density studies in the last decade, much remains to be done to characterize their relevant properties (electric and optical) in the solid state. A pair of isostructural materials currently under investigation are 2-(N-prolinol)-5-nitropyridine (PNP) and N-(4-nitrophenyl)-L-prolinol (NPP), both of which have second order NLO coefficients one or two orders of magnitudes greater than typical inorganic materials such as KTP. Charge density analyses have already been reported for NPP, but we are revisiting that material, along with PNP, to critically test a number of novel approaches to the estimation of linear and non-linear optical properties using constrained wavefunctions fitted to the X-ray diffraction data.¹ The basic theory will be summarized and, along with the usual charge density outcomes, we will present effective molecular polarizabilities and crystal refractive indices, and compare the results with theoretical estimates, and with other experimental data. Trends observed will be compared with results already obtained for urea, benzene and 2-methyl-4-nitroaniline (MNA).

(1) Whitten, A.E.; Jayatilaka, D.; Spackman, M.A. *J. Chem. Phys.* 2006, 125, 174505.