Towards calculating and interpreting the linear and second-order nonlinear optical properties of molecular crystals

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In this contribution it is shown that modest calculations combining first principles evaluations of the molecular properties with electrostatic interaction schemes to account for crystal environment are reliable for predicting and interpreting the experimentally-measured electric linear and second-order nonlinear optical susceptibilities within the experimental error bars. This is illustrated by considering two molecular crystals, namely: 2-methyl-4-nitroaniline (MNA) and 4-(N,N-dimethylamino)-3-acatamidonitrobenzene (DAN) [1]. A good agreement between theory and experiment is achieved providing the electric field effects originating from the electric dipoles of the surrounding molecules are accounted for. On the other hand, the intermolecular interactions determine the geometry and thus the linear and nonlinear optical responses. This study also highlights i) the key role of the geometry on the $\chi^{(1)}$ and $\chi^{(2)}$ responses, ii) the impact of the crystal environment on the geometries, iii) the role of electron correlation on the linear and nonlinear responses of the molecular crystals, iv) the good performance of the MP2 method to evaluate static properties, in combination with B3LYP to describe the frequency dispersion effects. A second illustration deals with the two anil crystals, [N-(4-hydroxy)-salicylidene-amino-4-(methylbenzoate) and N-(3,5-di-tert-butylsalicy- lidene)-4-aminopyridine, which can switch between a enol (E) and a keto (K) form [2].

[1] Seidler, T., Stadnicka, K., Champagne B., in preparation.
[2] Ségérie, A., Castet, F., Kanoun, M.B., Plaquet, A., Liégeois, V., Champagne B. *Chem. Matter*, 23:3993-4001, 2011.