VIBRATIONAL VS ELECTRONIC POLARIZABILITY AND FIRST HYPERPOLARIZABILITY OF SOME PUSH-PULL METAL PORPHYRINS

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At the microscopic level, the linear and nonlinear optical properties are governed by the dipole polarizability and hyperpolarizabilities. Nowadays, an intense research has been devoted to the design of new materials with large nonlinear optical properties. A particular attention has been given to synthesize efficient and stable organic chromophores.
Since the publication, by Bishop and Kirtman in the beginning of the 1990s, of the simple formulas for the caculation of the vibrational components of the dipole polarizabily and hyperpolarizabilities a particular attention has been given to evaluation of these contributions to the electric properties.
We report here a new set of engineering criteria for large molecular first-order NLO responses by varying the central metal ions in a porphyrin- based NLO chromophore structural moiety. A systematic study of the hyperpolarizabilities of metal porphyrins, where M = Zn, Ni and Fe is reported for the first time. The role played by the metal electronic structure in determining the dimension of the molecular first hyperpolarizabilities of these complexes have been studied at the DFT level. The magnitude of the two contributions to the first hyperpolarizability are compared to that of the typical chromophore, the p-nitroaniline (PNA).
The static vector first hyperpolarizability β^{v}_{vec}+β^{e}_{vec} have been evaluated at B3LYP/6-31G** to be equal in a.u. to 1299, 1377, 1692, and 1100 for the complexes Por-Fe, Por-Ni, Por-Zn, and for PNA, respectively. The individual normal mode contribution to the vibrational first hyperpolarizability have been determined in the case of the three considered complexes.