Theoretical investigation of the second-order nonlinear optical response of collagen – signatures of the triple helix structure

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Second-harmonic imaging microscopy (SHIM) is a high-resolution biomedical imaging technique, which has been developed to get contrast enhancement of non-centrosymmetric molecular arrangements. Campagnola and Loew [1] have reported that the first biological second harmonic generation (SHG) imaging experiment was done by I. Freund *et al.* [2] in 1986 on the collagen of rat-tail tendon. Measurement of the second-order hyperpolarizability of the collagen triple helix by Hyper-Rayleigh scattering (HRS) experiment was later performed by Deniset-Besseau *et al.* [3] who characterized the first hyperpolarizability (β) of the collagen I from rat-tail as well as of a short triple-helix model peptides $[(\text{Pro-Pro-Gly})_{10}]_3$ (PPG10). They concluded that the collagen large second-order nonlinear optical response originates from the tight alignment of a large number of small and weakly efficient harmonophores, presumably the peptide bonds, resulting in a coherent amplification of the nonlinear signal.

In this contribution we employ theoretical chemistry methods to calculate and to analyze the first hyperpolarizability of PPG10. The calculations are carried out by adopting the ONIOM method in combination with the TDHF or TDDFT method, which allows assessing the impact of electron correlation on the first hyperpolarizability. The different β tensor components are analyzed. In particular the first hyperpolarizability is decomposed into its dipolar and octupolar contributions and the depolarization ratio is calculated. This enables to unravel the origin of the β responses and to describe how the three intertwined helices participate to the total β.

[1] Campagnola, P. J., Loew, L. M. *Nat. Biotech.*, 21 (11):1356-1360, 2003.
[2] Freund, I., Deutsch, M., Sprecher, A. *Biophys. J.*, 50 (4):693-712, 1986.
[3] Deniset-Besseau, A., Duboisset, J., Benichou, E., Hache, F., Brevet, P.-F., Schanne-Klein, M.-C. *J. Phys. Chem. B*, 113 (40):13437-13445, 2009.