TWO-PHOTON CIRCULAR DICHROISM: A RESPONSE THEORY APPROACH TO NON-LINEAR PROPERTIES OF CHIRAL SYSTEMS

BRANISLAV JANSÍK,[§] HANS ÅGREN,[£] ANTONIO RIZZO[§]

[§] Istituto per i Processi Chimico Fisici del Consiglio Nazionale delle Ricerche, Area della Ricerca di Pisa, loc. San Cataldo, Via Moruzzi 1, I-56124, Pisa, Italy

[£] Theoretical Chemistry, Royal Institute of Technology, Roslagstullsbacken 15, SE-10691, Stockholm, Sweden

As main subject of the talk, the feasibility of calculations of two-photon circular dichroism (TPA-CD) by means of response theory will be demonstrated and discussed. The results from sample applications, involving the calculation of residues of appropriate frequency dependent mixed electric dipole-electric quadrupole-magnetic dipole quadratic response functions within a density functional theory model will be presented. The dependence of the results of the choice of the origin will be analyzed in some detail. The results indicate that the structural content of TPA-CD spectra is very different from both normal circular dichroism and two-photon absorption, thus highlighting a unique fingerprinting functionality for chiral species. Combined with increased penetrability of the infrared exciting light and the confocal nature of two-photon absorption, this makes TPA-CD a useful tool for biomolecular identification.

If time allows, another aspect of non-linear interaction of light with matter studied these days by the speaker will be introduced, in particular the insurgence of phenomena of circular and axial birefringence induced by polarized light in pump and probe optical experiments. The results obtained by accurate ab initio coupled cluster calculations (involving up to cubic frequency dependent response functions) for some reference achiral and chiral molecules will be presented.