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Editorial

Special Issue of Symmetry: "Recent Advances in Linear and Nonlinear Optics"

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In this Special Issue, invited researchers elaborate on 'Recent Advances in Linear and Nonlinear Optics', demonstrating how sensitive light–matter interactions are concerning symmetry. Through research articles and reviews, physicists, chemists, experimenters and theoreticians here exploit the (non)linearities of the dielectric response of molecules and nanostructures to probe their chemical features or, in return, to shape the light.

The symmetry sensitivity and the subsequent surface specificity of (non)linear optical techniques arise from the tensor structure of the dielectric response functions which relate the excitation electric field(s) with the polarization of matter [1]. Contrary to scalar functions describing isotropic phenomena, the mathematics of tensors conceptually enables the description of the response of matter in any direction (in 3D space) as a combination of different electric field contributions associated with different light beams and light polarization states. Researchers explicitly show how UV-visible, IR, Sum-Frequency Generation (SFG) and Raman spectroscopies all derive from the same tensor formalism, and then draw the consequences for experiments in terms of symmetry-related selection rules.

Henceforth, it is possible to assess the orientation and to identify the composition of a mixture of molecules adsorbed on surfaces by IR, Raman and SFG spectroscopies [2], and to quantify the sensitivity of each regarding their abilities to unmix the spectral signatures of the different chemical species. There is thus evidence that polarized Raman spectra are the most sensitive when the polarity of the molecular orientation is known, while even-order processes like SFG are required when there is ambiguity in the orientation polarity. Researchers here account for the complementarity between polarized Raman scattering, which gives access to numerous spatial projections due to its rank-4 third-order tensor response function, and sum-frequency generation, intrinsically surface-specific and symmetry-sensitive as a second-order dielectric response.

Interestingly, the symmetry-related selection rules that proper to second-order processes like SFG can be bypassed as soon as the sum-frequency generation results from the quadrupolar response of matter, instead of the dipolar one. This is the case in Second Harmonic Scattering (SHS). Typically, dipolar SHS is physically forbidden within centrosymmetrical materials, contrary to quadrupolar SHS. It is therefore possible to benefit from the competition between the two processes in order to differentiate liquid suspensions of molecular dyes on the basis of their (non-) centrosymmetric spatial arrangement [3]. By modeling the molecules as point-like nonlinear dipoles, researchers are able to account for experimentally characterized suspensions of dye aggregates, thus describing the collective organisation of molecular systems at the nanoscale.

In parallel, at the molecular scale, theoreticians benefit from Density Functional Theory (DFT) to study the second-order hyperpolarizability of complex molecules like polyoxometalates [4]. Such theoretical studies provide useful insights for experimenters as it enables the identification of the chemical features which significantly contribute to the nonlinear behavior of the molecules. Especially, the donor/acceptor character of the functional groups,

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as well as the hybridization states of the composite atoms and the subsequent nature of the chemical bonds (σ, π), critically influence the strength of the second-order response. This paves the way for studying the coupling of two molecules and more to draw near to real systems, like colloidal suspensions and adsorbed molecules.

Subsequently, at the nanoscale, it is possible to perform a quantitative analysis of composite or hybrid systems made of molecules/nanoparticles interfaces designed for optical (bio or chemical) sensing with an improved detection threshold at a low cost. By taking profit of quantum properties of small CdTe Quantum dots (QDs~3.4 nm diameter), researchers use advanced nonlinear optical Two-Colour Sum-Frequency Generation (2C-SFG) spectroscopy to check the hypothesis of the existence of a dipolar coupling from QD excitons to vibrations in their molecular environment to explain enhanced molecular sensitivity [5]. They demonstrate this physical process by comparing the dipolar coupling strength between the close chemical ligands of QDs with a farther molecular monolayer by highlighting $1/r^3$ spatial dependence compatible with dipole–dipole interactions.

As a matter of fact, plasmonics remains a growing research field for sensing thanks to the manufacturing of various metal nanomaterials, by adjusting at will the symmetry properties of plasmonic devices as discussed by researchers: rhombohedral arrays of nanoparticles, nanoholes (elliptical and circular). Recent developments in nonlinear plasmonics based on nanosystems in this review [6] show that symmetry breaking of their electronic properties increases dramatically the molecular sensitivity of nonlinear second-order processes such as those encountered in SHG and SFG spectroscopies. Another prominent developing research field related to symmetry breaking of electronic properties lies in chiral plasmonics based on (meta)materials allowing to specifically probe Left-circular or Right-circular light polarization taking account of bi-dimensional or three-dimensional effects. A comparison of the performances of various plasmonic devices is equally presented and discussed.

Conversely, by using plasmonic nanostructures of various sizes and shapes, it is possible to tune the light polarisation as a function of the LSPR response in favored directions. Researchers report in an extensive way the importance of the choice of a specific axis of symmetry for nanomaterials of increasing size and apply it to selected applications [7]: single nanosphere and dimers, trimers, nanorods, nanowires, nanoholes and nanoellipses, nanoprisms and nanotriangles, nanocrescents, hybrid plasmonic nanostructures. The monitoring of light polarisation states is therefore addressed through multifunctional metamaterials allowing polarisation conversion, from linear to: cross polarisation, left and right circular polarisation with chiral materials such as helical metamaterials. It allows us to design novel devices for real-life applications or overcome fundamental size and bandwidth limitations encountered in engineering based on conventional optics. Finally, a section is dedicated to the role of polarisation in magnetic-plasmonic nansotructures, considering multiple potential applications based on magneto-optics and magnetoplasmonics: Faraday effect and Inverse Faraday effect, magneto-optics Kerr effect, Magnetic plasmon resonances, SHG, magnetic circular dichroism.

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