Coordination Chemistry Reviews xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Computational studies of the nonlinear optical properties of organometallic complexes

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ARTICLE INFO

Article history:
Received 31 October 2017
Received in revised form 11 February 2018
Accepted 12 February 2018
Available online xxxx

Keywords:
Density functional theory
Computational methods
Nonlinear optics
Hyperpolarizabilities
Alkynyl complexes

ABSTRACT

Computational methods for calculating the molecular nonlinear optical (NLO) properties of molecules are reviewed, with an emphasis on clarifying the strengths and weaknesses of the various approaches. A brief introduction to the theory of NLO effects is provided, and a summary of the key experimental techniques for the determination of molecular first hyperpolarizabilities is included, with discussion of their advantages and disadvantages. Applications of semi-empirical methods and density functional theory in developing structure–quadratic NLO property relationships for organometallic complexes (and particularly metal alkynyl complexes) are reviewed.

Contents

Abbreviations: AC, alternating current or asymptotically correct; ADF, Amsterdam density functional; AM1, Austin model 1 semi-empirical method; au, atomic units; BBO, β-barium borate; CC, coupled-cluster; CHF, coupled Hartree–Fock; CI, configuration interaction; CNDO, complete neglect of differential overlap; CPHF, coupled–perturbed Hartree–Fock; CPKS, coupled–perturbed Kohn–Sham; CT, charge transfer; DC, direct current; DFT, density functional theory; DZ, double ς; DZP, double ς plus polarized; EFISH, electric field-induced second-harmonic generation; EOM-CC, equation-of-motion CC; DFG, difference-frequency generation; ERM, external reference method; FF, finite-field; GGA, generalized gradient approximation; HRS, hyper-Rayleigh scattering; ICT, intramolecular charge transfer; INDO, intermediate neglect of differential overlap method; INDO/S, INDO/spectroscopic approximation; IRM, internal reference method; KDP, potassium dihydrogen phosphate; KTP, potassium titanyl phosphate; LBO, lithium triborate; LDA, local-density approximation; LLCT, ligand-to-ligand charge transfer; LMCT, ligand-to-metal charge transfer; LR, long-range; LRC, LR corrected; MBPT or MP, many-body perturbation theory; MCSCF, TDMCSCF, MCTDHF, MCRPA, (time-dependent) multiconfiguration self-consistent field; MLCT, metal-to-ligand charge transfer; MNA, 2-methyl-4-nitroaniline; MP2, second-order Møller–Plesset perturbation theory; NLO, nonlinear optical; OR, optical rectification; PA, parametric amplification; PNA, *p*-nitroaniline; PPP, Pariser–Parr–Pople method; QZ4P, core triple-ς, valence quadruple-ς plus quadruply polarized; RPA, random-phase approximation; RS, range-separated; SFG, sum-frequency generation; SHG, second-harmonic generation; SIE, self-interaction error; SOPPA, second-order polarization propagator approximation; SOS, sum-over-states; SR, short-range; TDCHF or TDCPHF, time-dependent coupled (perturbed) Hartree–Fock; TDDFT, time-dependent DFT; TDHF, time-dependent Hartree–Fock; THG, third-harmonic generation; TLM, two-level model; TPA, two-photon absorption; TZP, core double-ς, valence triple-ς plus polarized; TZ2P, core double-ς, valence triple-ς plus doubly polarized; ZINDO, Zerner's intermediate neglect of differential overlap method.

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https://doi.org/10.1016/j.ccr.2018.02.007
0010-8545/

1. Introduction

Nonlinear optics deals with phenomena arising from light-induced changes in the optical properties of materials. The interaction of light with a nonlinear optical (NLO) material gives rise to new optical fields with altered properties (e.g., phase, frequency, amplitude, polarization, path, etc.) [1–4]. The high-intensity electromagnetic fields required are usually supplied by lasers, so routine observation of NLO phenomena was only possible after the advent of the laser in 1960 [5]. Modern nonlinear optics began with the first demonstration of second-harmonic generation shortly thereafter [6], but several NLO effects had been proposed or demonstrated beforehand (e.g., the Kerr or quadratic electro-optic effect, the Pockels or linear electro-optic effect [7], Raman scattering, two-photon absorption (TPA) [8], two-photon excitation [9], etc.). Following demonstration of the first working laser [5,10] and the first demonstration of second-harmonic generation [6], several other nonlinear optical effects (e.g., third-harmonic generation (THG), sum-frequency generation (SFG), difference-frequency generation (DFG), optical rectification, etc.) and the theoretical framework to describe the NLO phenomena were developed and demonstrated in quick succession [11,12].

NLO-efficient materials continue to be of intense interest, the research being given strong impetus by a plethora of applications. Organometallic complexes are of particular interest for reasons summarized below. The experimental studies have been complemented by computational approaches because the latter can not only post-rationalize the outcomes of experimental studies, but can also suggest fruitful experimental targets, and in addition can probe structural modifications accessible with difficulty experimentally. This review summarizes computational studies of the NLO properties of organometallic complexes, and includes a discussion of some materials considerations, a summary of the theoretical background to NLO phenomena, and a description of the experimental and computational methods that have been employed to investigate organometallics.

1.1. Material considerations

Nonlinear effects arise from the interaction of intense electric fields with nonlinear optical media. Materials with significant NLO properties have various technological applications such as data storage, optical computing, optical communication, optical switches, frequency generation, etc. [2,4,13,14]. Materials which provide large as well as fast NLO responses are desirable for practical devices, and the search for novel, efficient, photon-manipulating materials continues unabated because there is no material thus far which is suitable for all types of NLO applications.

Inorganic materials are usually robust with excellent thermal stability, and inorganic crystals were the initial choice for NLO materials, Franken et al. [6] observing the first example of second-harmonic generation when a ruby laser was directed at a quartz crystal. Subsequently, KTP (potassium titanyl phosphate), $LiNbO_3$, and $LiTaO_3$ were used for frequency conversions. Borate crystals have a high damage threshold and a broad transparency region, two critical material requirements for NLO device applications; LBO (lithium triborate) and BBO (β-barium borate) are the two most popular NLO crystalline materials from the borate family. LBO, BBO and KDP (potassium dihydrogen phosphate) crystals have found applications in third-harmonic generation of Nd:YAG lasers. Some chalcopyrite crystals such as $AgGaS_2$, $AgGaSe_2$, and $ZnGeP_2$ have been shown to be applicable for NLO uses in the infrared [15]. However, many NLO applications require fast responses and, in general, inorganic NLO crystals suffer from slow response times (usually of the order of nanoseconds) and little architectural flexibility [16].

Organic crystals represent another interesting class of NLO materials [4,17,18]. Bulk nonlinearities of organic crystals can be directly related to the optical nonlinearity of the molecular constituents, and the molecular structure can be used to optimize the nonlinearity, which is mostly derived from π-electron redistribution. As a result, organic crystals generally exhibit faster response times (of the order of femtoseconds) than inorganic crystals, for which lattice distortions or the dynamics of charge carriers lead to slower nonlinear responses [17,19,20]. In addition to fast response times, the advantages of organic crystals over inorganics include ease of fabrication, exceptionally large NLO responses, and ease of processing to films [21,22].

Organic molecules with electron releasing and withdrawing groups linked through a π-conjugated system have been found to exhibit strong quadratic NLO responses. However, most organic molecules crystallize in centrosymmetric space groups for which bulk second-order NLO effects (e.g., second-harmonic generation) vanish, although the molecular second-order response may be non-zero, e.g., *p*-nitroaniline (PNA) [22]. In contrast, 2-methyl-4-nitroaniline (MNA), for example, has a very large bulk material

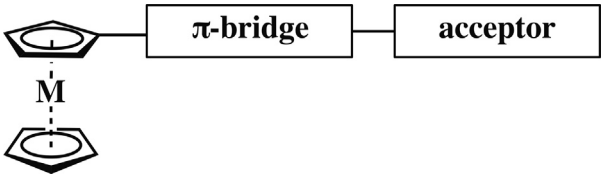

Fig. 1. Metallocenyl complex (M = metal (commonly Fe)).

Please cite this article in press as: M.S. Kodikara et al., Computational studies of the nonlinear optical properties of organometallic complexes, Coord. Chem. Rev. (2018), https://doi.org/10.1016/j.ccr.2018.02.007