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Density functional theory calculations on η^5-monocyclopentadienylnitrilecobalt complexes concerning their second-order nonlinear optical properties

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Abstract

Density functional theory calculations were performed to determine first static hyperpolarizabilities (β) of model complexes $[CoCp(H_2PCH_2CH_2PH_2)(p\text{-}NCC_6H_4R)]^{2+}$. The results show that these complexes have low hyperpolarizabilities which are due to weak electronic coupling between the organometallic fragment and the nitrile ligands. It was shown that in these complexes the electronic excitation responsible for second-order non-linear optical response is a ligand to metal charge transfer. The results also show the inverse relationship between the first hyperpolarizability and the corresponding electronic transfer energy gaps.

Keywords: Density functional theory; Non-linear optics; Hyperpolarizability

1. Introduction

Materials possessing nonlinear optical (NLO) properties are of technological importance in areas such as optical communications, optical computing and data storage [1–6]. The research on materials with these properties was initially focused on inorganic crystals and semiconductors and later on organic systems [1–11]. During the investigations of organic molecules for NLO, experimental and computational investigations utilizing quantum theory afforded useful insights concerning the molecular structural requirements necessary to induce large optical nonlinearities. Recently, organometallic complexes are attracting increasing attention in this field, mainly on second order nonlinear optical (SONLO) properties [12–17]. Unlike organic molecules, whose optical nonlinearities have been extensively studied by computational methodologies using both semi-empirical and ab initio methods, organometallic systems have received much less attention due to the difficulty in calculation reliable hyperpolarizabilities in the presence of transition metal atoms. ZINDO has been the most widely used program to calculate SONLO coefficients of organometallic compounds [17–21]. A more reliable approach, using the density functional theory (DFT) method is less explored but has been increased in the recent years [22–31].

Experimental work on η^5-monocyclopentadienyliron, ruthenium, nickel and cobalt complexes with *p*-substituted benzonitrile chromophores showed the fundamental role played by the organometallic fragment in their second-order nonlinear optical response [32]. However, for the cobalt complexes, the experimental β's were found to be not reliable due to their decomposition during the experimental essay, leading to overestimated first hyperpolarizabilities. Nevertheless, these results were still lower than those obtained for the ruthenium and iron counterparts and were explained by the absence of π back-donation in the former

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