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Third order nonlinear optical polarisability induced by real electronic excitations in transition metal diimine and dithiolene complexes

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Abstract

The organo-transition metal complexes (Ni or Pt)bis(3,4-toluenediimine), Ni-bis(3,4-benzophenonediimine) and Ni-bis(1-phenyl-2-butyl-1,2-dithiolene), which are generally considered to be good candidates for third order nonlinear optical (NLO) applications, have been examined by sub-picosecond induced transparency measurements. The electronic decay times are around 2 ns for each of the compounds, while the orientational relaxation happens in the 100 ps range. High third order NLO parameters have been previously reported from degenerate four wave mixing experiments, but not confirmed by several other techniques. This disparity in results is clarified here in terms of noninstantaneous contributions from real electronic excitations.

1. Introduction

The transition metal diimine and dithiolene complexes studied here have recently attracted considerable attention because of their interesting third order nonlinear optical (NLO) properties. Due to their strong charge transfer (CT) bands in the region from 700 to 800 nm they are expected to show a strong near-resonant enhancement of the third order NLO polarisability (γ) for wavelengths in the near infrared. By varying the substituents, the donor groups (S or NH) or the central metal atom, the position of the absorption band can be tuned to achieve the optimum ratio between near-resonant enhancement of $\chi^{(3)}$ and absorption losses [1,7]. In this way similar transition metal complexes have been synthesized with absorption maxima varying from 633 up to 1400 nm [4,5]. Indeed, it was concluded from a series of experimental studies using the degenerate four wave mixing (DFWM) technique [1,4,7] that for some of the compounds the figures of merit are acceptable for all-optical switching devices, especially for Ni-bis(1-phenyl-2-butyl-1,2-dithiolene) [9].

However, very different results have been obtained by different techniques. While DFWM yielded γ values up to 2×10^{-44} m^5 V^{-2} for some of these compounds [9,4,7] (and even 8.6×10^{-43} m^5 V^{-2} for excitation near the absorption maximum [13]), results obtained with third harmonic generation (THG) are typically three orders of magnitude smaller [6], and quadratic electro-optic measurements also indicate much smaller values [11,12]. Experiments performed by Oliver et al. [1] using DFWM have shown that the measured $\chi^{(3)}$ depends strongly on

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