EFFECTIVE EXCITED STATES FOR $\chi^{(3)}$ IN A SYMMETRIC CONJUGATED MOLECULE

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INTRODUCTION

Several studies have been carried out to search for centrosymmetric finite-size conjugated molecules with large third-order susceptibility, $\chi^{(3)}$ \(^1-4\). We have reported symmetrical molecules i.e. terephthal-bis-(4-N,N-diethylamino aniline) and 2,5-dichloro-terephthal-bis-(4-N,N-diethylamino aniline)\(^4\), which are referred to as SBA and SBAC, and also reported urethane polymer with finite length $\pi$-conjugation, which is symmetrically substituted triazo dyes, as an optical waveguide material\(^5\). This polymer is abbreviated as PU-STAD. The $\chi^{(3)}$ values of SBA, SBAC and PU-STAD compare well with conjugated polymers. For short centrosymmetric conjugated molecules such as finite polyene, theoretical numerical investigations of the electronic mechanism have been carried out \(^6,7\), and the effect of the Ag excited state is described. The THG $\chi^{(3)}$ is expressed as a product of one sequence of four successive transition moments\(^8-10\).

$$\chi^{(3)}_{ijkl} = \frac{1}{4} \sum_{i,m,n} \left[ \frac{1}{6} P_{ijkl} \frac{\mu^i_{gl} \mu^j_{lm} \mu^k_{mn} \mu^l_{ng}}{(E_{ig} - 3\hbar\omega)(E_{mg} - 2\hbar\omega)(E_{ng} - \hbar\omega)} + \ldots \right]$$

where $\mu$ is a transition dipole moment, $l,m,n$ are excited or ground states, and $E_{ig}$ is an excitation energy of state $l$ with a dumping factor. For finite polymer and some similar molecules, the sequence including an Ag excited state, i.e. G - 1Bu - (excited)Ag - 1Bu - G, is very effective because of the large transition moment between Bu and Ag excited states. In the long wavelength nonresonant region, this is numerically proved by theoretical research\(^7\). Even in a resonant case such as two photon or three photon resonance where denominator of eq.(1) is a complex value, it can be said by an approximation that large transition moment between Bu and Ag excited states enhances $\chi^{(3)}$ too. It is important to know for each molecule, what sort of Ag excited state is effective among the many Ag states. In the case of a finite polyene, high lying Ag state is effective\(^7\). For some conjugated polymers, a low lying Ag excited state is effective\(^11\). However, the mechanism that determines the effective Ag state has not been clarified yet.

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In this work, we have calculated the substitution effect of the molecular type in Fig. 1 to clarify the mechanism. The donors are amino and the X and Y positions are carbon or nitrogen atoms. Molecular orbitals for these molecules are calculated by semiempirical CNDO method and additional configuration interaction. We look into the substitution effect upon orbital shape and the effective excited states for THG $\chi^{(3)}$. If a low-lying $A_g$ excited state is effective, it should be better for $\chi^{(3)}$, because low excitation energy decreases the denominator of $\chi^{(3)}$ more than high lying ones. We have found that a low lying $A_g$ excited state is effective for some substitution conditions.

![Diagram](image.png)

**Figure 1.** Molecular type and substitution effect.

A (Finite phenylene vinylene)  
B  
C  
D (SBA)  
E  
F

**Figure 2.** The molecules calculated in this work.