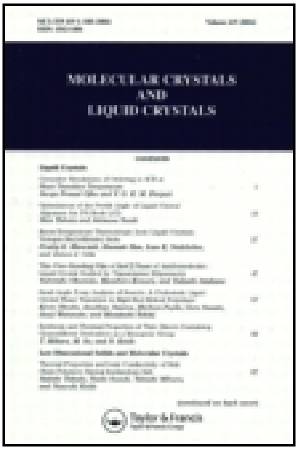

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Theoretical Studies on Nonlinear Optical Properties of Organometallic Conjugated Systems I: Static Third-Order Hyperpolarizabilities of First-Transition-Metal and Metal-Methylene Cations

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THEORETICAL STUDIES ON NONLINEAR OPTICAL PROPERTIES OF ORGANOMETALLIC CONJUGATED SYSTEMS I: STATIC THIRD-ORDER HYPERPOLARIZABILITIES OF FIRST-TRANSITION-METAL AND METAL-METHYLENE CATIONS

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Abstract Various *ab initio* electron-correlation methods with several extended basis sets were applied to calculate static third-order hyperpolarizabilities (γ's) of first-transition-metal and metal-methylene cations. We found remarkable dependences of γ's on electron correlations and basis sets for these systems. The results also indicated that γ's of these systems were largely influenced by their electronic configurations.

INTRODUCTION

To date, a lot of theoretical and experimental approaches have been made to the search for nonlinear optical (NLO) materials.[1-5] Organic NLO materials have attracted much attention because of their low cost, fast and large nonlinear optical response, synthetic flexibility, high optical damage thresholds, and intrinsic tailorability.[6] Most of the reported organic NLO materials are pπ-electron conjugated systems. On the other hand, organometallic conjugated systems, which are known by their unique characteristics such as diversity of metals, oxidation states, ligands, and geometries, have not been sufficiently investigated, though such systems are expected to possess large NLO properties because of their pπ-dπ conjugation.

In recent years, intensive experimental studies on optical non-linearities of organometallic compounds have started.[6] In contrast, theoretical studies by *ab initio* methods have been rarely performed because of their computational difficulties. Namely, huge computational resources are required since extended basis sets and high-level electron-correlation methods are essential to obtain reliable NLO properties for these systems. However, recent progress of computers enable us to calculate hyperpolarizabilities of small- and intermediate-size organometallic systems by *ab* *initio* methods with extended basis sets and high-level electron-correlation methods.

In the present work, we investigate dependences of static third-order hyperpolarizabilities (γ's) on basis sets and electron correlations and elucidate relations between γ's and orbital configurations for first-transition-metal and metal-methylene cations. *Ab initio* calculations using various basis sets and electron-correlation methods were applied to calculate γ's for these systems. To our knowledge, this is the first attempt to *ab initio* study on non-linear optical properties for organometallic conjugated systems.

CALCULATION METHODS

It is well known that hyperpolarizabilities calculated by *ab initio* methods depend remarkably on both the quality of basis sets and the electron-correlation methods. However, these dependencies for organometallic compounds have not been clarified yet. Therefore, as a beginning, we performed *ab initio* calculations of γ's of first-transition-metal and metal-methylene cations by using various basis sets and electron-correlation methods.

(1) Geometries and Electron Configurations for Metal-Methylene Cations

Figure 1 illustrates the coordinate axes for the $M{=}CH_2^+$ systems. The bonding, non-bonding and antibonding σ orbitals are constructed from the $2p_z$ AO of methylene CH_2, and the $3d_{z^2}$ and 4s AOs of the transition metal M. The bonding and antibonding π-MOs are given by a linear combination of the $2p_y$ AO of CH_2 and the $3d_{yz}$ AO of M. The perpendicular π-MOs are similarly given by the $2p_x$ AO of CH_2 and the $3d_{zx}$ AO of M. The remaining two 3d AOs of M, $3d_{x^2-y^2}$ and $3d_{xy}$, form δ_1 and δ_2 MOs, respectively. The orbital configurations for the ground states of $M{=}CH_2^+$ cations[8] are summarized in Table I.

For $NiCH_2^+$, C-H distance (R(C-H)) and M-C-H angle were optimized by UHF, and M-C distance (R(M-C)) was determined by UMP4 with R(C-H) and M-C-H angle previously estimated. For other metal ions, R(M-C)'s were optimized by UMP4.

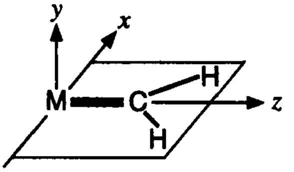

FIGURE 1 Coodinate axes for transition-metal-methylene cations.

TABLE I States and orbital configurations for the ground states of first transition-metal-methylene cations and configurations of transition-metal cations.[8]

Systems	States	$d^l s^m$ a)	Orbital configurations b)							
			σ	π	π^*	σ^*	$\pi_\perp$	δ_1	δ_2	σ_n
$TiCH_2^+$	$^2A_1$	d^2s^1	2	2	0	0	0	1	0	0
VCH_2^+	$^3B_2$	d^3s^1	2	2	0	0	1	1	0	0
$CrCH_2^+$	$^4B_1$	d^5	2	2	0	0	1	1	1	0
$MnCH_2^+$	$^5B_1$	d^5s^1	2	2	0	0	1	1	1	1
$FeCH_2^+$	$^4B_2$	d^6s^1	2	2	0	0	1	2	1	1
$CoCH_2^+$	$^3B_1$	d^7s^1	2	2	0	0	2	2	1	1
$NiCH_2^+$	$^2A_1$	d^8s^1	2	2	0	0	2	2	2	1
$CuCH_2^+$	$^1A_1$	d^{10}	2	2	0	0	2	2	2	2

a) Configurations of transition-metal cations.

b) σ: a_1, π: b_1, σ^*: a_1, π^*: b_1, $\pi_\perp$: b_2, δ_1: a_1, δ_2: a_2, σ_n: a_1.

(2) Basis Sets

Basis sets employed for transition metals were Huzinaga's split-valence MIDI (53321/521/41).[9] To examine basis sets dependencies, we also employed four extended basis sets: MIDI augmented by 4p polarization functions, MIDI+p (53321/5211/41), MIDI+p augmented by 4d functions, MIDI+pd (53321/5211/411), MIDI+pd augmented by 4f functions, MIDI+pdf (53321/5211/411/1), MIDI+pdf augmented by more diffuse d and f functions, MIDI+pdfdf (53321/5211/4111/11). These diffuse functions' exponents are summarized in Table II.

For carbon atom, the standard split-valence 6-31G augmented by diffuse p and d functions, 6-31G+pd, was used. This is usually used to reproduce reliable hyperpolarizabilities for organic molecules. For hydrogen atom, 6-31G was used since contributions of hydrogen atoms to γ's are not important in this study.

(3) Electron Correlations

Coupled Hartree-Fock (CHF) finite-field (FF) method was applied to calculate static γ's. This method can be used as a starting point to include higher-order electron-correlation corrections by using conventional various post Hartree-Fock calculation programs. In this work, we employed UHF based Møller-Plesset nth-order purtur-

TABLE II Exponents of diffuse functions for transition metals.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
diffuse p, d, f	0.073	0.071	0.077	0.092	0.098	0.085	0.088	0.090
more diffuse d, f	0.025	0.027	0.027	0.025	0.026	0.023	0.022	0.022

bation (MPn), quadratic configuration-interaction (QCI) and coupled-cluster (CC) methods.

RESULTS AND DISCUSSIONS

(1) γ's of Metal Cations

Table III shows γ_{zzzz}'s for first-transition-metal cations calculated by UHF and CCSD(T) methods with various basis sets. It is clear that standard split-valence basis sets (MIDI) fail to provide sufficiently large $|\gamma|$'s and to include electron-correlation corrections sufficiently. An addition of polarization 4p functions remarkably increases the $|\gamma|$'s by HF and CCSD(T). Effects of polarization 4d and 4f functions are essential for some metal cations, while additions of more diffuse d and f functions slightly modify γ's by HF and CCSD(T) methods. We can, therefore, conclude that CCSD(T) method with split-valence plus polarization p, d and f basis sets, MIDI+pdf, are at least required to obtain sufficiently converged γ's for first transition metal cations.

As can be seen from the CCSD(T) results of Ti$^+$, V$^+$, Cr$^+$, Co$^+$, Ni$^+$ and

TABLE III γ_{zzzz}'s of first-transition-metal cations.[a)]

		Basis sets				
Metal ions[b)]	Methods	MIDI	+p	+pd	+pdf	+pdfdf
Ti$^+$	HF	0.124	−196.	−30.2	−31.1	−27.9
$(3d^24s)$	CCSD(T)	0.765	−128.	184.	162.	149.
V$^+$	HF	0.195	24.0	33.2	34.6	31.7
$(3d^4)$	CCSD(T)	0.409	76.9	113.	119.	100.
Cr$^+$	HF	0.025	4.11	5.72	6.93	7.14
$(3d^5)$	CCSD(T)	0.024	7.20	13.0	14.0	16.4
Mn$^+$	HF	0.003	−78.0	−36.2	−35.7	−34.9
$(3d^54s)$	CCSD(T)	0.002	−79.0	−35.8	−36.5	−34.5
Fe$^+$	HF	0.003	−71.4	−37.7	−36.2	−35.0
$(3d^64s)$	CCSD(T)	0.002	−72.0	−41.4	−36.4	−34.5
Co$^+$	HF	0.010	2.81	4.36	4.97	1.55
$(3d^8)$	CCSD(T)	0.450	−1.59	7.50	7.57	4.05
Ni$^+$	HF	0.006	0.987	2.03	2.52	2.51
$(3d^9)$	CCSD(T)	0.010	5.33	6.21	7.70	7.45
Cu$^+$	HF	0.003	0.477	0.906	1.20	1.21
$(3d^{10})$	CCSD(T)	0.004	1.24	2.37	3.05	3.01

a) in 10^2 a.u.

b) Valence-orbital configurations are represented in parentheses.

c) γ of ethylene calculated by CCSD(T) with 6-31G+pd basis set is 10.6×10^2 a.u..

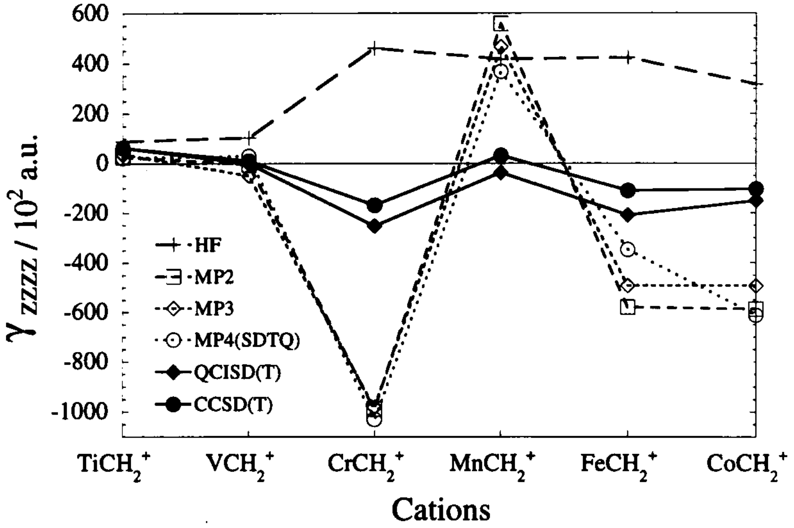

FIGURE 2 γ_{zzzz}'s for various metal-methylene cations.

Cu^+, $|\gamma|$'s dramatically increase for the systems with small number of electrons occupying $3d\,(3d^n$: $n \leq 4)$, while $|\gamma|$'s decrease for those with large number of electrons occupying $3d\,(3d^n$: $n \geq 5)$. It is also suggested from the results of Mn^+ and Fe^+ that an electron in $4s$ orbital has a large negative contribution to γ.

(2) γ's of Transition Metal-Methylene Cations

Figure 2 shows γ_{zzzz}'s of transition metal-methylene cations calculated by various *ab initio* methods. It is noteworthy that these values are quite different from those of metal cations. They exhibit remarkeble electron-correlation dependences. The γ's by HF method are different from CCSD(T) even in sign, and MPn method overestimates electron-correlation correction. Therefore, QCISD(T) and/or CCSD(T) are found to be required to obtain sufficiently converged γ.

We can also see large dependences of γ's on the orbital electronic configurations summarized in Table I. For example, an electron in δ_2 orbital seems to provide a negative contribution to γ. Although relations between γ's and orbital configurations are very complicated, this problem could be discussed by partitioning total γ's to contributions from each natural orbital with the aid of hyperpolarizability density analysis.[10]This analysis is in progress in our laboratory.

CONCLUDING REMARKS

The present ab initio calculations of first transition metal and metal-methylene cations have revealed the following characteristics:
(1) CCSD(T) and QCISD(T) methods with split-valence plus polarization p, d and f basis sets (MIDI+pdf) are at least required to calculate γ's of first transition metals and metal-methylene cations semiquantitatively.
(2) Electrons in $3d$ orbitals provide positive contributions to γ's of transition metal ions, while an electron in $4s$ orbital provides negative contribution. When the number of electrons in $3d$ orbitals are less than 5, their contributions are quite large.
(3) γ's of transition metal-methylene cations are significantly different from those of metal cations.
(4) γ's of transition metal-methylene cations largely depend on the orbital electronic configurations.

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