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ARTICLE in SYNTHETIC METALS · FEBRUARY 1997

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Theoretical studies on nonlinear optical properties of organometallic conjugated systems III: second hyperpolarizabilities of Mn(I)-carbene systems

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Abstract

Various ab initio electron-correlation methods are applied to calculate second hyperpolarizabilities (γ 's) of MnCH^+ , MnCH_2^+ and MnCH_3^+ . These systems showed significant dependences on the electron correlations. MnCH_3^+ , which have a single Mn-C bond, exhibited the larger γ than MnCH^+ and MnCH_2^+ , which have weak π bonds.

Keywords: (Ab initio quantum chemical methods and calculations, Hyperpolarizabilities, Transition metals)

1. Introduction

Recent years, studies on nonlinear optical (NLO) properties of organometallic systems have been intensively carried out [1]. These systems are expected to possess unique NLO properties because of their unique bond nature. Very recently, we applied various ab initio electron-correlation methods for calculation of the second hyperpolarizabilities (γ 's) of transition-metal triplet-methylene systems and revealed that these systems exhibited large γ 's compared to ethylene, which has as similar size as metal-methylene, and γ 's for these systems had large dependences both on electron-correlations and orbital electron configurations [2].

In the present work, we carried out ab initio calculations to obtain static γ 's for Mn(I)-carbene systems, i.e., MnCH^+ , MnCH_2^+ and MnCH_3^+ . The former two systems are thought to have weak π bonds [4], so these systems seem to be triple, double and single bonded systems, respectively. Our objective is to clarify the relationship between the bond nature and the γ 's for these systems.

2. Calculations

Coordinate axes for MnCH_x^+ ($x = 1, 2, 3$) cations are illustrated in Fig. 1. We confine our attention to the γ 's in the direction of the bond axes, i.e., γ_{zzz} 's. Static γ_{zzz} 's are calculated by using numerical finite-field (FF) method. The total energies of molecules in the presence of external electric field is calculated by ab initio coupled Hartree-Fock (CHF) method. Unrestricted HF (UHF) wave functions are employed in the calculations and electron-correlation effects are included by using post HF methods such as Møller-Plesset n th order perturbation (MP n), quadratic configuration interaction (QCI) and coupled-cluster (CC) methods. A basis set used for a metal is Huzinaga's MIDI [5] augmented by diffuse p , d and f functions, MIDI+pdf. For carbon and hydrogen atoms, the standard split-

valence 6-31G augmented by diffuse p , d functions, 6-31G+pd, and 6-31G basis sets are used, respectively. These ab initio calculations are performed by using GAUSSIAN 92/DFT program package [6].

To analyze the calculation results, hyperpolarizability density analysis [3] is employed. The γ_{zzz} density is defined as the third order derivative of the electron density with respect to the z component of the external electric field. Figure 2 illustrates how to understand a γ_{zzz} density plot. White and black circles represent the regions with positive and negative γ_{zzz} density, respectively. When the arrow from the positive to the negative coincides with the positive direction of the z axis, the arrow means positive contribution to the γ_{zzz} . The arrow with the opposite direction means the negative contribution.

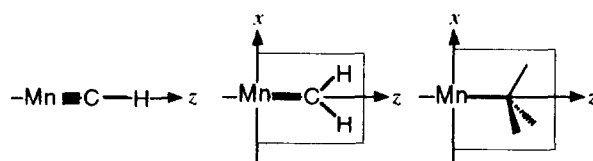


Fig. 1. Coordinate axes for MnCH^+ , MnCH_2^+ and MnCH_3^+ .

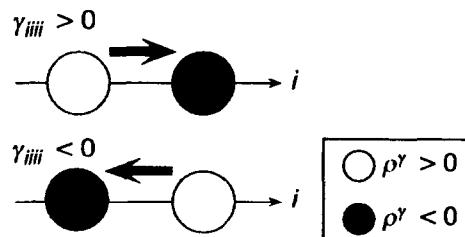


Fig. 2. Schematic diagram of a γ_{zzz} density plot.

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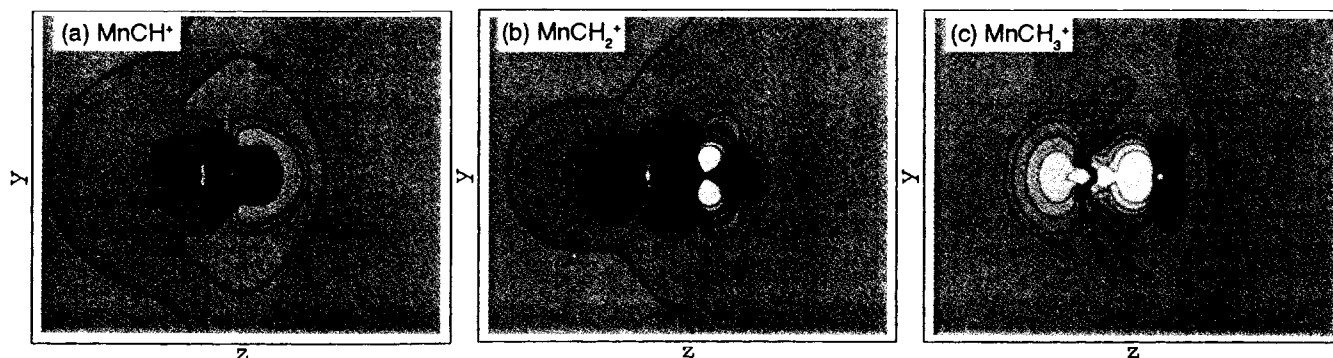
Table 1

 γ_{xxx} 's of Mn(I)-carbene cations calculated by using various electron-correlation methods.^{a,b}

Systems	UHF	MP2	MP3	MP4DQ	MP4SDTQ	QCISD	CCD	CCSD	CCSD(T)
MnCH ⁺	28.3	-47.0	-42.6	-35.0	-48.9	-13.6	-38.8	1.08	0.74
MnCH ₂ ⁺	49.3	21.3	14.8	13.4	5.66	5.03	14.9	2.92	0.14
MnCH ₃ ⁺	-80.7	-60.1	-47.4	-40.7	-8.35	11.7	-42.3	14.3	14.2

a In 10³ a.u.

b MIDI+pdf, 6-31G+pd and 6-31G basis sets are used for manganese ion, carbon and hydrogen atoms, respectively.

Fig. 3. γ_{xxx} densities on the yz planes for MnCH_x⁺ (x = 1, 2, 3) cations calculated by the QCISD method.

3. Results and discussion

3.1 Electron-correlation dependences

Table 1 gives the γ_{xxx} 's for MnCH_x⁺ systems (x = 1, 2, 3) calculated by various electron-correlation methods. These results indicate that the methods including only the double (D) and quadruple (Q) excitation effects (MP2, MP3, MP4DQ and CCD) cannot reproduce the CCSD(T) value. The single excitation (S) and triple excitation (T) effects in the MP4 level modify the γ_{xxx} 's by MP4DQ for MnCH₂⁺ and MnCH₃⁺, whereas that effect does not show appropriate modification for MnCH⁺. From the CCD and CCSD results, the contributions of the high-order S effects are positive to the γ_{xxx} 's for MnCH⁺ and MnCH₃⁺, while that is negative to the γ_{xxx} for MnCH₂⁺. The effects of perturbatively included T in the CCSD(T) method have negative contributions to the γ_{xxx} 's, especially significant for MnCH₂⁺. The QCISD method is shown to well reproduce the CCSD γ_{xxx} for MnCH₂⁺ and MnCH₃⁺, but give a wrong sign for MnCH⁺. From the results mentioned above, high-order S and D effects have to be included, i.e., the CCSD method are required in order to obtain sufficiently converged γ_{xxx} 's.

3.2 Bond-nature dependences

The CCSD(T) results indicate that the order of the γ_{xxx} 's is MnCH₃⁺ >> MnCH⁺ > MnCH₂⁺, namely, the γ_{xxx} for the system without π bond is much larger than that for the system with π bonds. From this result, electrons in the π orbitals are shown to provide negative contribution to the γ_{xxx} 's so that the γ_{xxx} 's for MnCH⁺ and MnCH₂⁺ become smaller compared to MnCH₃⁺. The γ_{xxx} plots shown in Fig. 3 support this hypothesis. Figure 3 (c) depicts that large white region (positive γ_{xxx} density) is placed on the left side of the plots and γ_{xxx} is large positive value. To the contrary, Fig. 3 (a) and 3 (b) show that large black region (negative γ_{xxx} density) is placed on the left side. As can be seen from Fig. 2, large black regions on

the left of the system provide negative contributions to the γ_{xxx} . Thus, we can see that the electrons in the π orbitals provide negative contributions.

4. Concluding remarks

The present ab initio calculations have revealed that the γ_{xxx} 's for MnCH_x⁺ systems (x = 1, 2, 3) have large dependence on electron correlations, and the electrons in the π orbitals provide negative contributions.

Acknowledgement

The authors gratefully acknowledge a financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No. 06101004).

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