

## Nonlinear Optical Properties of Tri-nuclear Transition Metal Clusters M-( $\mu$ -S)<sub>s</sub>-M' (M=Mo, W; M'=Cu, Ag, Au)

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**Abstract:** The static polarizabilities and the second-order hyperpolarizabilities of a series of tri-nuclear metal cluster models MS<sub>4</sub>(M'PPh<sub>3</sub>)<sub>2</sub>(M'PPh<sub>3</sub>) (M=Mo,W; M'=Cu, Ag, Au) have been calculated within the first-principle theoretical framework. The model clusters have two fragments of rhombic units and it is the charge transfer from one of these moieties to the other that is responsible for nonlinear optical property. This kind of electronic delocalization, differentiated from that of planar  $\pi$ -system, is very interesting and is worthy for further investigation.

**Keywords:** Transition metal cluster, nonlinear optical property, finite-field approach, density functional theory method.

Some of the transition metal cluster compounds show promising nonlinear optical (NLO) responsibilities<sup>1</sup>, which may apply in optical absorption, self-focusing, refraction and optical limiting effects. However, the traditional trial-and-error method is insufficient to achieve satisfactory novel material research. Theoretical investigations provide detailed understanding of the structure-property relationship and are helpful to the design and simulations of novel NLO materials. In this paper, a series of typical tri-nuclear metal clusters Mo(W)-S(Se)-Cu(Ag, Au) are modeled and geometrically optimized. The static polarizabilities and hyperpolarizabilities of these molecular clusters are then calculated using the finite-field (F-F) approach and the first-principle density functional theory method. We try to reveal the origin of the NLO properties of this family of transition metal cluster compounds.

The calculation of the static polarizabilities and hyperpolarizabilities of a molecule is straightforward in a F-F approach<sup>2</sup>. The explicit expressions for the diagonal tensor components,  $\alpha_{ii}$ ,  $\gamma_{iii}$  and  $\gamma_{ijj}$  are listed below:

$$\alpha_{ii} = \frac{1}{(\sigma^2 - \sigma^4)F^2} \{ \sigma^4 [\Delta E(F_i) + \Delta E(-F_i)] - [\Delta E(\sigma F_i) + \Delta E(\sigma F_i)] \}$$

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$$\gamma_{iii} = \frac{12}{(\sigma^4 - \sigma^2)F^4} \{ \sigma^2 [\Delta E(F_i) + \Delta E(-F_i)] - [\Delta E(\sigma F_i) + \Delta E(\sigma F_i)] \}$$

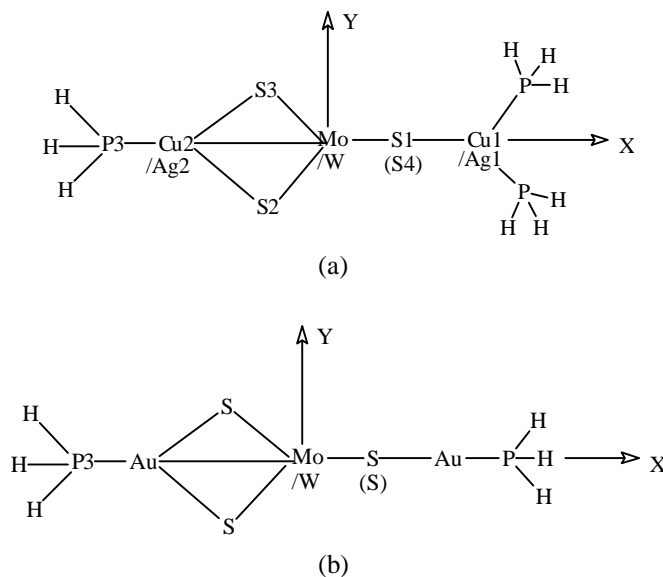
$$\gamma_{ijj} = \frac{1}{F^4} \{ 2[\Delta E(F_i) + \Delta E(-F_i) + \Delta E(F_j) + \Delta E(-F_j)] - [\Delta E(F_i, F_j) + \Delta E(-F_i, F_j) + \Delta E(F_i, -F_j) + \Delta E(-F_i, -F_j)] \}$$

where  $F_i$  corresponds to a finite field the  $i$  direction,  $i=x, y$  or  $z$ . We set median values of  $F=0.0050$  a.u. and  $\sigma F=0.0030$  a.u. with  $\sigma = 0.6$ . The isotropic scalar values for  $\alpha$  and  $\gamma$  averaged from their tensor components are defined as,

$$\bar{\alpha} = \sum_i \alpha_{ii} / 3; \quad \bar{\gamma} = \sum_{ij} \gamma_{ijj} / 5$$

The six molecular clusters of Mo(W)-S(Se)-Cu (Ag, Au) family are (I)  $\text{MoS}_4\text{Cu}(\text{PH}_3)_2\text{Cu}(\text{PH}_3)_3$ , (II)  $\text{MoS}_4\text{Ag}(\text{PH}_3)_2\text{Ag}(\text{PH}_3)_4$ , (III)  $\text{MoS}_4\text{Au}(\text{PH}_3)\text{Au}(\text{PH}_3)_5$ , (IV)  $\text{WS}_4\text{Cu}(\text{PH}_3)_2\text{Cu}(\text{PH}_3)_4$ , (V)  $\text{WS}_4\text{Ag}(\text{PH}_3)_2\text{Ag}(\text{PH}_3)_6$  and (VI)  $\text{WS}_4\text{Au}(\text{PH}_3)\text{Au}(\text{PH}_3)_7$ , which come from the typical tri-nuclear Mo/W-Cu/Ag-S/Se transition metal cluster compounds<sup>3-7</sup> by simplifying the ligands (PPh<sub>3</sub>) with (PH<sub>3</sub>). The model clusters are then geometrically optimized. We divide the six clusters into two groups. The group 1 includes mode I, II, IV and V, and the group 2 has III and VI. Each group has similar structure. All six models are placed in such a coordinate system that the central Mo(W) atoms coincide with the origin. (see **Figure 1**).

**Figure 1** Coordinate system and molecular structures of (a) model clusters I, II, IV and V. (b) models III and VI.



All calculations were carried out using the Gaussian 98 package<sup>9</sup>. We adopted B3LYP as the gradient-corrected exchange potential in the density functional theory calculation. For all the atoms involved, the basis set LanL2DZ set applied. A full set of 34 energy differences  $\Delta E(F_i, F_j, F_k)$  was calculated, followed by the independent components  $\alpha_{ij}$  and  $\gamma_{ijkl}$ .

One features of Mo/W-S transitional metal cluster compounds is that the building blocks of quadrangular  $M-(\mu-S)_2-M'$  ( $M=Mo, W; M'=Cu, Ag, etc.$ ) has extensive  $\pi$ -electron-delocalization over the four-atom ring. The  $p$  orbitals on bridging S atoms largely contribute to frontier molecular orbitals. The  $M-(\mu-S)$  bond was the main factor in stabilizing the cluster systems. Selected results of calculated linear polarizabilities and the second-order hyperpolarizabilities are given in **Table 1**. In this study, the first-order hyperpolarizabilities are of less concern. This is because the selected Mo(W)-S(Se)-Cu(Ag, Au) cluster compounds are centrosymmetric, and it is the third-order optical nonlinearities that are of greatest interest to us. The model clusters which are nearly centrosymmetric, have negligible dipole moments and the first hyperpolarizabilities, and thus we only list the results of polarizabilities and the second-order hyperpolarizabilities in **Table 1**.

We find quite large  $\gamma$  values in the **Table 1**, for example,  $\bar{\gamma}$  of cluster V is about  $1.2 \times 10^5 a.u.$ , which is about  $60 \times 10^{-36}$  esu. They are quite promising to apply in the NLO process.

**Table 1** Calculated results of polarizability and the second-order hyperpolarizability of the six model tri-nuclear Mo(W)-S-Cu (Ag, Au) clusters

	Group 1			Group 2		
	I	II	IV	V	III	VI
$\alpha_{xx}$	342.114	351.160	330.573	341.878	393.979	383.060
$\alpha_{yy}$	205.633	220.322	203.452	217.669	175.192	173.122
$\alpha_{zz}$	177.981	187.918	176.214	184.979	175.356	173.182
$\alpha$	241.909	253.134	236.747	248.175	248.176	243.121
$\gamma_{xxx}$	325710	469310	292397	426557	409873	393967
$\gamma_{yyy}$	35370	44693	35247	45053	4480	4707
$\gamma_{zzz}$	7643	7613	7343	6947	3953	3717
$\gamma_{xyy}$	43602	55400	40280	52152	5080	6253
$\gamma_{yyz}$	3309	3731	3027	3397	2360	1898
$\gamma_{zzx}$	8411	15003	9570	16208	5258	6322
—	95873	133977	88148	124414	88740	86267

The second-order hyperpolarizability components  $\gamma_{iii}$ , as well as those of linear polarizability  $\alpha_{ii}$ , are related to the quantities  $[\Delta E(F_i) + \Delta E(-F_i)]$ , which we believe to reflect the susceptibility of electronic systems. Given an appropriate electronic field strength ( $F$ ) and a suitable factor ( $\sigma$ ), the absolute values of  $\alpha_{ii}$  and  $\gamma_{iii}$  will be definitely determined by a difference  $\{\sigma[\Delta E(F_i) + \Delta E(-F_i)] - [\Delta E(\sigma F_i) + \Delta E(-\sigma F_i)]\}$  or  $\sigma[\Delta E(F_i) - \Delta E(\sigma F_i)]$ , which relates to the electronic susceptibility of the molecule in  $i$  direction. Fortunately, the selected model construction is so clear that it permits us to explore the relations between the external field perturbation effects on the electronic structures and

the third-order hyperpolarizabilities in depth. Models I, II, IV and V in the group 1 have similar structures and properties. First, one may be impressed by the aeolotropism of molecular properties. Components containing  $x$  subscripts are much larger than those with only  $y$  or  $z$  indices. In each model cluster,  $\gamma_{xxxx} > \gamma_{yyyy} > \gamma_{zzz}$  ladder with one order of magnitude and  $\gamma_{xyy} \gg \gamma_{zzx} > \gamma_{yyz}$ . These orders indicate the sulfido-bridged transitional metal cluster cores, which are arranged along the  $x$  axis, are predominantly responsible for the third-order optical nonlinearity. Second, the two terminal phosphine ligands coordinated to  $M'_1$  in group 1, though important to  $\gamma_{yyy}$  ( $y$  axis is along the direction of line P1- P2), contribute much less to  $\bar{\gamma}$ . To understand this, it may be worthy to note that, in our calculations we find that for cluster II,  $\Delta E(F_x, F_y) - \Delta E(F_x, -F_y) = 0.2547$ ,  $\Delta E(-F_x, F_y) - \Delta E(-F_x, -F_y) = 0.2279$  while  $\Delta E(F_x, F_y) - \Delta E(-F_x, F_y) = -1.5251$ ,  $\Delta E(F_x, -F_y) - \Delta E(-F_x, -F_y) = -1.5519$ , the former differences are much less pronounced than the latter, indicating the electric fields act more effectively along  $M'_1$ -M- $M'_1$  ( $x$  direction) than along line P1-P2 ( $y$  direction).

Several meaningful conclusions can be drawn from these studies. The model molecules, although can be divided into two subgroups, are alike in that the structure of two fragments of rhombic units  $M-(\mu-S)_2-M'$  ( $M=Mo, W$ ;  $M'=Cu, Ag, Au$ ), perpendicular to each other, and joined by sharing the node atom  $M$ . It is the charge transfers from one of these moieties to the other in these characteristic sulfido-transitional metal cores that are responsible for polarizabilities and hyperpolarizabilities. This kind of electronic de-localization, differentiated from that of planar  $\pi$ -system, is interesting and worthy of further investigations. The structural effects on properties are important. In subgroup 1, considerable second-order nonlinearities are exhibited. The element substitution effect of  $Mo$  and  $W$  is weak, while that of  $Cu$  and  $Ag$  is considerable. For convenience, an overall order can be written as,  $\gamma_{xxxx}(Mo-Ag) > \gamma_{xxxx}(W-Ag) > \gamma_{xxxx}(Mo-Au) > \gamma_{xxxx}(W-Au) \geq \gamma_{xxxx}(Mo-Cu) \geq \gamma_{xxxx}(W-Cu)$  and  $\gamma(Mo-Ag) \sim \gamma(W-Ag) > \gamma(Mo-Au) \sim \gamma(W-Au) \sim \gamma(Mo-Cu) \sim \gamma(W-Cu)$ .

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