Effect of separation on second-order hyperpolarizability of two silver nanoclusters

Ying Chang, Weiqi Li, Yongyuan Jiang *

Department of Physics, Harbin Institute of Technology, Harbin 150001, China

A R T I C L E   I N F O

A B S T R A C T

We present a study on dielectric response of Ag_{14} nanocluster dimer using first principles methods. The interaction energy, (hyper)polarizability of dimer are predicted under various separations of the two identical Ag_{14} nanoclusters. The appropriate separation makes the second-order hyperpolarizability of Ag_{14} dimer is about 70 times larger than the Ag_{14} monomer. The increase of polarizability and hyperpolarizability is ascribed to reconfiguration of molecular electronic state from Ag cluster monomer to dimer. Nonlinear response is more susceptible to the steady intermediate state compared to linear response. The crucial transitions contributed to hyperpolarizability are assigned to be from highest occupied molecular orbitals to the lowest unoccupied molecular orbital (HOMOs-LUMO) of nanocluster dimer. Binding character of LUMO plays an important role in determining nonlinear optical properties.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Noble-metallic surface and particles sustaining coherent electron oscillations knows as surface plasmon polaritons can lead to the enhancement of electromagnetic fields has been investigated for applications in nonlinear optics (NLO) processes, such as Raman scattering [1,2] and harmonic generation [3]. In recent decades, nanoparticles have been a hot topic of extensive studies because of the outstanding physical and chemical properties against those of atoms or bulk materials [4–8]. The microscopic hyperpolarizability strongly reflects macroscopic nonlinear susceptibility tensor [9–11], and provides a wealth of transition characteristics of various electronic states as well on the relative nonlinear optical response [12].

Advances in single particle synthesis and fabrication techniques have recently allowed for studies of noble-metal nanoparticle [13]. Now the preparation method of packing nanocluster includes pointing optical fiber [14–16] and lithographic techniques [17,18]. The latter approach affords flexible control of the size and shape of nanoparticles. Intermolecular interaction is found to cause a very large enhancement of the nonlinear polarizabilities in theory and experiment [19]. The interaction between two closely packed metal nanocluster has been the subject of various theoretical and experimental studies, and many interesting phenomena on dimers or trimers have been observed recently [20–22]. The nonlinear susceptibility of nanocluster dimers depends strongly on interactions between particles as the distance changes. Due to the inversion symmetry, the second-order nonlinear response of silver nanoclus-

ter dimer is negligible. Nevertheless, symmetry does not affect the linear and third-order nonlinear response of such metal nanostructures. Hence, we expect strong second-order hyperpolarizability compared to two independent monomers because of the interaction between nanoparticle dimers. Linear dielectric response of silver nanoparticle dimers was predicted by using density functional theory (DFT) for Ag_{14} [23,24]. However, it is also interesting and important to study the third-order nonlinear optical effect of silver nanoparticle dimer based on first principles methods because it is responsible for third harmonic generation, two-photon resonances, and other nonlinear optical phenomena.

In this Letter, we present a detailed study of the electronic coupling between two silver nanoclusters using DFT. Evolution of the polarizability and second-order hyperpolarizability of Ag_{14} dimers as a function of the separation between the two nanoparticles is explored in detail. There is a strong dependence of the nonlinear dielectric response on the separation. At an appropriate separation, redistribution of electronic configuration of ground state and excited state cause high second-order hyperpolarizability from Ag_{14} monomer to dimer.

2. Computational details

The silver nanoparticle dimer consists of two identical nanoparticles with 14-atoms, which is a fragment of silver bulk in the face-centered cubic structure. The monomer was firstly optimized, using PBEPBE functional with Lanl2DZ basis set [25,26], as implemented in the software of Gaussian 03 package [27]. On basis of the DFT-optimized geometries, TD-PBEPBE/LanL2DZ is employed to calculate the absorption spectra of Ag nanoparticle dimer.

As shown in Fig. 1, the axis of dimer is assumed along the y direction and the size of Ag cluster monomer is 0.686 nm.

* Corresponding author. Tel.: +86 0451 86414130.
E-mail address: jiangyy@hit.edu.cn (Y. Jiang).
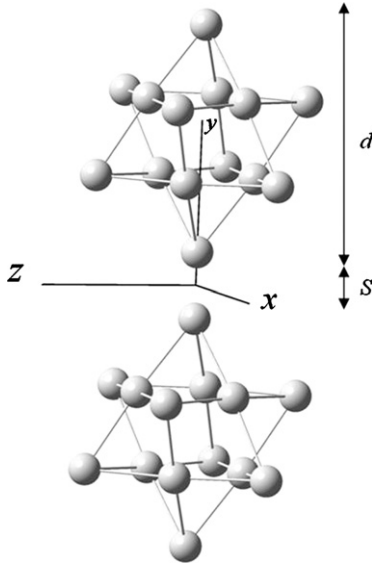
Fig. 1. Atomic configuration of Ag_{14} dimers. The dimer axis is along y axis as a function of separation S.

Table 1
Mean (hyper)polarizabilities, longitudinal (hyper)polarizabilities, and anisotropy polarizabilities of monomer and dimers at different separations between monomers.

	α_{yy}	$\bar{\alpha}$	$\Delta\alpha$	γ_{yyyy}	$\bar{\gamma}$
Monomer	588.7	588.6	0.1936	3199995.3	2719995.2
Dimer-3	2588.2	1592.5	1493.6	31999996.3	5039999.1
Dimer-4	2211.9	1477.6	1101.4	297600010.5	74480004.0
Dimer-5	1686.7	1311.5	562.9	441599986.5	87039986.1
Dimer-6	1402.4	1223.6	268.2	185600016.3	33840000.1
Dimer-7	1297.2	1193.8	155.1	44800006.4	14480012.8
Dimer-8	1257.9	1184.8	109.6	12799995.6	14079987.9
Dimer-9	1238.5	1181.6	85.4	6400005.1	5839990.6
Dimer-10	1226.4	1180.1	69.5	3199980.7	10160000.2

Fig. 2. Interaction energy of Ag_{14} dimers as a function of separation S. Insets: Charge distribution of dimer-3, dimer-8 and monomer. (For interpretation of the references to color, the reader is referred to the web version of this article.)

Considering the size of model system, the dimer under selected separation can reflect the physical nature of true systems. To characterize the dielectric response of the system, the polarizability in several discrete separations $S = 2$–10 Å is predicted and marked as dimer-S for simplicity. Among all the components of polarizability and hyperpolarizability, only the y component along the dimer axis is considered and it is sensitive to the dimer separation S. From the theoretical point of view, the molecular electronic polarizabilities can be defined in their static form by Taylor series expansion of the perturbed energy of a molecule (or atom) in the presence of a weak uniform external static electric field as follows [28,29]

$$E^P = E^0 - \sum_{\alpha} \mu_\alpha F_\alpha - \sum_{\alpha,\beta} \alpha_{\alpha\beta} F_\alpha F_\beta / 2 - \sum_{\alpha,\beta,\gamma} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma / 6$$
$$- \sum_{\alpha,\beta,\gamma,\delta} \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta / 24 + \cdots \quad (1)$$

E^P is the energy of the molecular (or atomic) system in the presence of the static electric field (F), E^0 is its energy in the absence of the field, μ_α corresponds to the permanent dipole moment of the system, $\alpha_{\alpha\beta}$ to the static dipole polarizability tensor (or linear polarizability), and $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ to the first- and second-order hyperpolarizability (or second- and third-order nonlinear polarizability), respectively. With appropriate choice of fields ($F = \pm 0.0005$ au and $F = \pm 0.001$ au), we calculated (hyper)polarizability by using finite-field (FF) method. The mean and anisotropy of the dipole polarizability can be written as [30]

$$\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (2)$$
$$\Delta\alpha = 2^{-1/2}\big[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2\big]^{1/2} \quad (3)$$

Eq. (1) can be used to extract the components of the hyperpolarizability tensor that are necessary to obtain the value of $\bar{\gamma}$. The mean second-order hyperpolarizability is defined in terms of the Cartesian components as follows [31]:
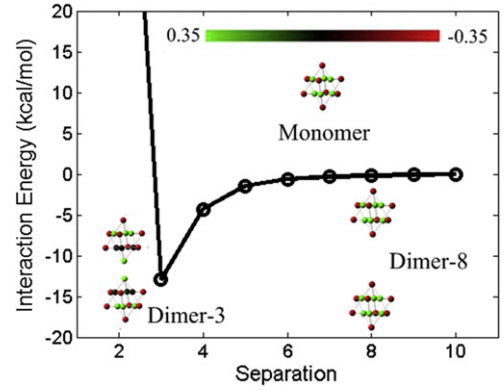
$$\bar{\gamma} = \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{xxzz}) \quad (4)$$

The longitudinal components, and mean (hyper)polarizabilities of monomer and dimers (with different separation between monomers) are presented in Table 1.

3. Results and discussion

The interaction energy between two nanoparticles *vs.* separation S is shown in Fig. 2. A dimer with high energy on potential energy surface is observed for $S = 2.0$ Å which is shorter than Ag–Ag bond distance and presents strong intermolecular repulsion. We do not consider this shorter distance configuration ($S = 2.0$ Å) when the evolution of (hyper)polarizability *vs.* the separation is investigated. With the increase of S, repulsion quickly decreases, and is taken over by intermolecular attraction, and gradually the interaction reduces to zero. Nature of interaction between clusters at various separation is different, from covalent bond to van der Waals interaction [32]. The insets of Fig. 2 are the corresponding spatial distributions of the charge distribution in dimer-3, dimer-8 and monomer, respectively. Shaded green indicates positive charge, while shaded red indicates negative charge. Dependent on the variation of separation, there is a dramatic redistribution of charge on nanoparticles. Compared with monomer, the charge distribution in dimer-8 reflects the configuration with very weak interaction between monomers. Such charge distribution is caused by the change of interaction between nanoparticles, which characterizes the optical response of the nanoparticles [33,34]. It have been found that plasmon oscillations have dramatic effect on the optical property of two nearly touching metallic nanospheres [35,36]. By pulling the particles away from each other, the electronic coupling between the sliver nanoparticle can be tuned to reach the optimal position for optical dielectric response.

Fig. 3 shows the evolution of the longitudinal components of linear polarizability α_{yy} and the mean polarizability of Ag_{14} dimer as a function of the separation S. The twofold monomer polarizability is also presented for comparison. That the maximal longitudinal component of linear polarizability α_{yy} occurs at dimer-3 and it decreases monotonically with increasing separation S. The longitudinal and mean polarizability converge to the corresponding