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Nonlinear Optical Properties of Molecularly Bridged Gold Nanoparticle Arrays

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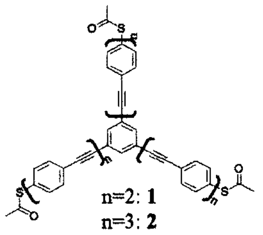
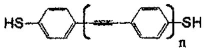
Methods for assembling metal nanoparticles into symmetrically and spatially well-defined architectures are important because new properties often emerge from the particle aggregate that are distinctly different from the corresponding isolated nanoparticles. For example, collective nanoparticle behaviors are responsible for large surface-enhanced Raman signals[1] and first hyperpolarizabilities[2] and the familiar red−blue color change currently being exploited in a number of colorimetric assays.[3] The success of many emerging nanoscale electronics technologies (e.g., single-electron devices, quantum cellular automata[4]) also will depend largely on the ability to organize nanoparticles and optimize capacitive or dipole coupling in the resulting assembly.

Collective nanocluster behaviors have traditionally been assessed using extended 2- or 3-dimensional nanocluster arrays prepared by (i) salt-induced aggregation,[2] (ii) Langmuir techniques,[5] (iii) surface assembly,[1] or (iv) crystallization.[6] Vance and co-workers, for example, utilized hyper-Rayleigh scattering (HRS) to interrogate aqueous suspensions of 13 nm diameter gold particles.[2] First hyperpolarizabilities (β) were found to surpass the best available molecular chromophores. Moreover, β increased more than 10-fold upon the addition of salt, likely due to the formation of non-centrosymmetric particle aggregates.[7] However, the fact that salt-induced aggregation does not lead to a preferred symmetry precluded a detailed account of structure−optical function relationships.

Methods for assembling gold and silver nanoparticle aggregates of well-defined symmetry and interparticle spacing have been developed previously.[8] These protocols employ thiol-functionalized phenylacetylene (PA) "templates" **1**−**5** whose symmetries dictate the symmetry of the resulting aggregate. Addition of substoichiometric amounts of a desired template to a solution of particles has yielded discrete particle dimers, trimers, or tetramers, with pseudo $D_{\infty h}$, D_{3h}, T_d, or D_{4h} symmetries, depending on the chosen molecular bridge.


n=2: **1**
n=3: **2**


n=1: **3**
n=5: **4**
n=7: **5**

Recognizing that for monodisperse spherical particles, a D_{3h}-symmetric trimer is the simplest non-centrosymmetric aggregate prompted us to investigate HRS of PA-bridged gold nanoparticle arrays. The results reported herein (i) confirm earlier TEM evidence of lowered symmetry for the arrays, (ii) reveal large second-harmonic responses from non-centrosymmetric trimers relative to centrosymmetric monomers and dimers, and (iii) show, for trimers, decreases in β with increasing interparticle distance. HRS theory and instrumentation have been described previously.[2,9] Briefly, HRS is incoherently scattered second harmonic light. For species in solution, it reports directly on β, without the need for electric-field alignment of the species. We employed the mechanically chopped output of a mode-locked Ti:sapphire laser (820 nm) as the incident light source. Nonlinear scattering was collected over a wide solid angle centered at 90°, passed through appropriate optical filters, and retrieved by lock-in amplification. Control experiments (detection monochromator successively set above, at, and below 2ω) established that the signals indeed were HRS, rather than two-photon-induced fluorescence responses.

Presented in Table 1 are HRS data for gold nanoparticle monomers, dimers, and trimers.[10] While trimer formation clearly increases the nonlinear scattering intensity, I, it has an almost negligible effect on the linear extinction spectrum.[8] (In contrast, the formation of large aggregates is well-known to exert a substantial influence upon the extinction spectrum, inducing features in the red and near-infrared region.) Figure 1 shows HRS intensities as a function of the square of the input power for 8 nm diameter gold monomers, dimers, and trimers. The linear relationship in each plot is indicative of HRS rather than residual coherent SHG. Also apparent in Figure 1 are the comparatively high nonlinear scattering efficiencies, per component nanoparticle, for trimers versus monomers and dimers. Note that dimers, like spherical monomers, are centrosymmetric objects.

To quantify the nonlinear behavior and facilitate benchmarking versus more familiar molecular chromophores, we have also reported first hyperpolarizabilities. While the description of β for molecular scatterers is unambiguous, a direct comparison to β values for nanoparticles might not be appropriate since the latter can contain tens or even hundreds of thousands of atoms.[11] A better comparison would be scattering efficiency per unit volume. Recognizing that the nonlinear scattering intensity scales as β^2, we suggest $\beta_{\text{particle}}{}^2$/atom (or $\beta_{\text{molecule}}{}^2$/atom) as an approximation to the desired volume-normalized quantity. Conventional first

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[1] (a) Chumanov, G.; Sokalov, K.; Gregory, B.; Cotton, T. M. *J. Phys. Chem.* **1995**, *99*, 9466. (b) Feilchenfeld, H.; Chumanov, G.; Cotton, T. M. *J. Phys. Chem.* **1996**, *100*, 4937. (c) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.

[2] For early HRS/nanoparticle reports, see: (a) Johnson, C. K.; Soper, J. A. *J. Phys. Chem.* **1989**, *93*, 7281. (b) Clays, K.; Hendrickx, E.; Triest, M.; Persoons, A. *J. Mol. Liq.* **1995**, 67, 133. (c) Baranov, A. V.; Inoue, K.; Toba, K.; Yamanaka, A.; Petrov, V. I.; Fedorov, A. V. *Phys. Rev. B Condens. Matter* **1996**, 53, R1721. (d) Vance, F. W.; Lemon, B. I.; Hupp, J. T. *J. Phys. Chem. B* **1998**, *102*, 10091. (e) Johnson, R. C.; Hupp, J. T. In *Metal Nanoparticles: Synthesis, Characterization, and Applications*; Feldheim, D., Foss, C., Eds.; Marcel-Dekker: New York, in press.

[3] (a) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607. (b) Mirkin, C. A. *Inorg. Chem.* **2000**, *39*, 2258.

[4] (a) Keating, C. D.; Feldheim, D. L. *Chem. Soc. Rev.* **1998**, *26*, 1. (b) Lent, C. S.; Tougaw, P. D. *J. Appl. Phys.* **1993**, *74*, 6227.

[5] Shiang, J. J.; Heath, J. R.; Collier, C. P.; Saykally, R. J. *J. Phys. Chem B* **1998**, *102*, 3425.

[6] Harfenist, S. A.; Wang, Z. L.; Alvarez, M. M.; Vezmar, I.; Whetten, R. L. *J. Phys. Chem.* **1996**, *100*, 13904.

[7] Enhanced HRS due to aggregation induced by pyridine has also been noted: Galletto, P.; Brevet, P. F.; Girault, H. H.; Antoine, R.; Broyer, M. *J. Phys. Chem. B*, **1999**, *103*, 8706.

[8] (a) Brousseau, L. C., III; Novak, J. P.; Marinakos, S. M.; Feldheim, D. L. *Adv. Mater.* **1999**, *11*, 447. (b) Novak, J. P.; Feldheim, D. L. *J. Am. Chem. Soc.* **2000**, *122*, 3979.

[9] Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1994**, *65*, 2190 and references therein.

[10] Solutions of dimers and trimers are invariably contaminated with unreacted monomer; thus, the HRS data for these species are corrected using TEM-derived concentrations of each aggregate.

[11] For example, the largest of the trimers here contains ~90000 atoms; β_{trimer} is $\sim 1 \times 10^{-24}$ esu per component nanoparticle.

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Table 1. HRS Data for Gold Nanoparticles and Arrays

scatterer[a]	I[b]	$\beta'/10^{-30}$ esu	D[c]
5 nm *m*	1.0	680 ± 30	2.8
5 nm *t***1**	4.9	1500 ± 210	2.2
5 nm *t***2**	4.5	1450 ± 150	2.3
8 m *m*	7.0	1800 ± 200	1.8
8 nm *d***3**	3.7	1300 ± 160	1.9
8 nm *d***4**	2.6	1100 ± 120	1.9
8 nm *d***5**	5.1	1530 ± 150	2.1
8 nm *t***1**	31	3800 ± 410	1.6
8 nm *t***2**	15	2700 ± 330	1.6
10 nm *m*	12	2400 ± 300	2.5
10 nm *t***2**	26	3500 ± 470	2.1

[a] *Component* nanoparticle diameters are given. *m* denotes monomer; *d* and *t* refer to dimer and trimer arrays. [b] Relative HRS intensity per component nanoparticle. [c] HRS depolarization ratio. Measurement uncertainties ranged from 0.05 to 0.12. ϵ_{820} is negligible.

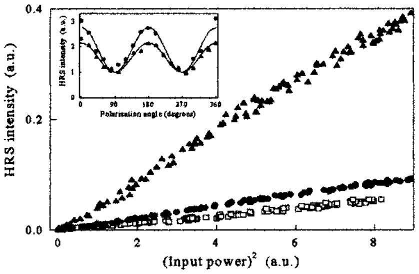

Figure 1. Relative HRS intensity of 8 nm trimer 1 (▲), dimer 3 (□), and monomer (●). Inset: HRS depolarization plot for 5 nm monomer (top) and trimer 1 (bottom).

hyperpolarizability units can be retrieved by defining the normalized or "per atom" hyperpolarizability as $\beta' = (\beta_{\text{particle}}{}^2/\text{atom})^{1/2}$. We report our data in this fashion (Table 1).

The observed β' values for the gold nanoparticles and, in particular, the trimeric particle assemblies, are as large or larger than those of the best molecular chromophores.[12,13] In part, the extraordinary values for the particles are a consequence of two-photon resonance interactions with the colloids' intense plasmon band; the values no doubt would be smaller under conditions of preresonance with the plasmon absorption band[14,15] In addition, the occurrence of quadrupolar scattering has been suggested as a partial explanation for the existence of nonzero HRS signals (from monomers), despite the particles' centrosymmetric crystal structure and near spherical shape.[14,16] Returning to the table, it is also evident that β' for the assemblies is particle size-dependent, increasing as the gold monomer diameter increases from 5 to 10 nm.[17]

Table 1 also lists depolarization ratios, D (the ratio of vertically-to horizontally polarized HRS, based on vertical incident polarization; see inset in Figure 1). The ratios observed for trimers are consistently smaller than for monomers, dimers, or randomly assembled large aggregates. For *molecular* scatterers, D reports on the point-group symmetry of the scatterers.[18] While the physics clearly is different for scattering by metal nanoparticles versus molecules, we suggest that here D is likewise reporting on the symmetry of the scatterer. Candidate symmetry-related explanations for the differences in D and in I include enhanced quadrupolar scattering and the onset of an octupolar scattering mechanism. The latter would require each trimer to behave as a single, unified chromophoric entity, even though the component particles are separated by ~2 nm. While difficult to envision for molecular chromophores, strong electromagnetic interactions over such distances are well established for metal nanoparticles.[19] Clearly, further theoretical work would be useful.

Finally, the distance dependence of electromagnetic communication between particles in PA assemblies was analyzed within the context of their β' values (Table 1). For trimers, β' decreases with increasing interparticle distance. Again, available theory for *linear* spectroscopy indicates that interparticle electromagnetic interactions for free-electron metals in this size regime will decay as a complex function of distance—with the interaction propagating farther for larger particles.[19] In contrast to electronic communication between linked molecular chromophores, the strength of the interparticle electromagnetic interaction is expected to be insensitive to linkage ligand conjugation, orientation, HOMO energy, and LUMO energy, as well as chromophore/linkage chemical interaction, instead depending only on the dielectric properties of the linkage ligand and any other intervening material (for example, interstitial solvent). Note that a similar correlation between nonlinear scattering intensity and distance is lacking for the centrosymmetric gold dimers, suggesting that here the particles are largely behaving as individual, rather than collective, nonlinear scatterers.

In conclusion, hyper-Rayleigh scattering spectroscopy has been used to measure collective nonlinear optical behaviors in gold nanoparticle arrays. Exceptionally large responses were observed. The findings indicate that both symmetry and distance are important in determining the nonlinear optical behaviors of nanoscale objects (free-electron metal particles) connected by molecular bridges.

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(12) The normalized hyperpolarizabilities in refs 7 and 17 for monomeric gold particles agree well with those found here once they are recast in terms of β' ($= [\beta^2/\text{atom}]^{1/2}$). The values reported in ref 2a are incorrectly described as β/atom; they are, in fact, β' values.

(13) For example, for the molecular chromophore [5-[[4′-(dimethylamino)-phenyl]ethynyl]-15[4″-nitrophenyl]ethynyl]-10, 20-diphenylporphinato]zinc-(II)—an exceptionally efficient system—the values of β and β' for $\mathbf{8}_{\text{inc}} = 1064$ nm are $\sim 5000 \times 10^{-30}$ and $\sim 520 \times 10^{-30}$ esu, respectively (LeCours, S. M.; Guan, H.-W.; DiMagno, S. G.; Wang, C. H.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1497.

(14) Antoine, R.; Brevet, P. F.; Girault, H. H.; Bethell, D.; Schiffrin, D. J. *Chem. Commun.* **1997**, 1901.

(15) The data in ref 14 indicate a precipitous drop in SHG efficiency as the second harmonic frequency is shifted away from resonance with the plasmon band. On the other hand, excitation profile studies of HRS from silver nanoparticles, reveal persistent nonlinear scattering (e.g., β' . 1000×10^{-30} esu) under preresonance conditions (Li, J.; Johnson, R. C.; Hupp, J. T.; Schatz, G. C., unpublished studies).

(16) Agarwal, G. S.; Jha, S. S. *Solid State Commun.* **1982**, *41*, 499.

(17) For monomeric scatterers, the Agarwal–Jha theory[16] predicts an increase in total scattering power with the square of the number of atoms, or equivalently, a linear increase in β' with the number of atoms. Galetto and co-workers (*Chem. Commun.* **1999**, 581) have also reported on the gold monomer particle size dependence of the HRS efficiency. If recast in terms of either I or β', the data indicate—consistent with the more limited study here—systematic increases with increasing number of atoms: I% (number of atoms)$^{1.5}$ or β' % (number of atoms)$^{0.75.}$

(18) See, for example: Kaatz, P.; Shelton, D. P. *J. Chem. Phys.* **1996**, *105*, 3918.

(19) For a representative theoretical study (linear spectra), see: Jensen, T.; Kelly, L.; Lazarides, A.; Schatz, G. C. *J. Cluster Sci.* **1999**, *10*, 295.