# Observation of a fifth order optical nonlinearity in 29 kDa Au@alkanethiol clusters

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## ABSTRACT

The optical nonlinearity in nanoclusters of Au@hexanethiol and Au@dodecanethiol has been investigated. From the mass spectra, each cluster is estimated to contain between 29 to 40 atoms of gold. The optical absorption spectra of the clusters are devoid of the plasmon absorption band, and show a gradual increase in absorbance towards the UV region. When excited with nanosecond laser pulses at 532 nm, an optical limiting behavior is observed, which fits to a three-photon absorption mechanism. We propose that this nonlinearity is caused by free carrier absorption subsequent to two-photon absorption taking place in the medium. The temporal dynamics of the nonlinearity reveals a fast process, with a lifetime of less than 2 picoseconds.

**Keywords:** metal nanoclusters, optical limiting, two-photon absorption, free carrier absorption, temporal dynamics.

## 1. INTRODUCTION

Optical properties of metal nanoparticles form an active area of current research, owing to their importance in photonics and nanotechnology [1,2]. A number of studies have shown that they are good optical limiters. However, the surface plasmon resonances found in metal nanoclusters can lead to saturable absorption-like behavior as well. Thus the nonlinear optical transmission in these materials is dependent on several factors, including the particle size.

In this work we have prepared nanoclusters of Au@hexanethiol and Au@dodecanethiol, having particle sizes in the range of 1 nm. The optical absorption spectra are devoid of the plasmon absorption band, and show only a monotonic increase in absorbance towards the UV region. The nonlinear optical transmission, when excited with 7 ns laser pulses, is investigated. The temporal dynamics of the nonlinearity also is studied using femtosecond pump-probe measurements.

## 2. SYNTHESIS AND CHARACTERIZATION

The synthesis of the clusters was carried out under ambient conditions by the Brust method [3], using hexanethiol and dodecanethiol as protecting species. Details of the synthesis are given elsewhere [4]. In short, 20 ml of 50 mM aqueous $HAuCl_4$ solution and 80 ml (4 mM) tetra-n-octylammonium bromide (TOAB) in toluene were mixed and stirred vigorously. Then 3 mM solution of the respective thiol (hexanethiol or dodecanethiol) in toluene was added and the resulting mixture was stirred for additional 20 min. Aqueous 10 mM sodium borohydride (10 ml) was introduced at once to the stirring mixture. The desired product was obtained after vigorous stirring for 12 h (hexanethiol) and ~2 days (dodecanethiol), respectively. The precipitate was filtered, redissolved in toluene and reprecipitated with excess propanol; the procedure was repeated twice to ensure that the excess disulfide/thiol was removed. At this stage, we adopted column chromatographic techniques for the separation of the required mass range. This precipitate was loaded onto silica column (60-120 mesh) and eluted by 5% ethyl acetate/hexane mixture. The eluted fractions are evaporated and the materials are collected as dry powders. The mass of the cluster of interest is confirmed to be 29 kDa by its MALDI (Voyager DE PRO Biospectrometry Workstation (Applied Biosystems) mass spectrum. UV/Vis spectroscopy (Perkin Elmer Lambda 25 UV/Vis spectrometer) also confirmed the presence of the desired clusters. The MALDI and optical absorption spectrum are given in Fig.1. No plasmon absorption is seen in the optical absorption spectrum. These results suggest that the present sample contains 29 kDa cluster compound exclusively. Similar MALDI and UV/VIS

results have been obtained for the 29 kDa-optimized preparations of Au@dodecanethiol using the same synthetic procedure.

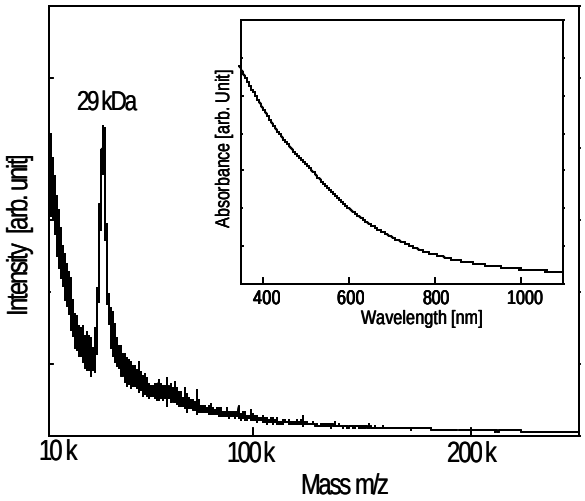


Fig. 1: MALDI-TOF spectrum of column separated Au@hexanethiol cluster compound with matrix indole acrylic acid (ratio 1:5) showing the presence of 29 kDa clusters exclusively. A minor peak due to the dimer formed during the ionization process is also seen. *Inset:* Optical absorbance spectrum of the same sample. As expected, the surface plasmon resonance is absent.

## 3. EXPERIMENTAL

To investigate the nonlinear transmission properties of the nanoparticles, we used 7 ns laser pulses from a frequency-doubled, Q-switched Nd: YAG laser (532 nm), which is operated in the single-shot mode. From beam profile measurements using the knife-edge method, the spatial intensity profile of the laser is found to be near-gaussian. The laser pulse energy reaching the sample is attenuated to about 37 microjoules, using neutral density filters. The fluence dependent transmission is measured using an open aperture z-scan set-up, which is automated. In the z-scan, the laser beam is focused using a lens, and the sample is translated along the beam axis (z-axis) through the focal region over a length, several times that of the confocal distance. At each position z the sample sees a different laser fluence, and the position dependent (ie, fluence-dependent) transmission is measured using a pyroelectric energy probe placed after the sample. The input energy of each pulse is measured by another calibrated pyroelectric detector. Data from the energy probes is used in the calculations, and the best numerical fit to the transmission equations is obtained. To investigate the possibility of induced scattering in the present samples, we did a few z-scans in which a photomultiplier tube (PMT) was used in addition to the existing detectors, to record the scattered radiation. The PMT was fixed at an angle of about 15 degrees to the beam axis, at a vertical distance of 5 cm from the pyroelectric probe that detects the transmitted beam. By mounting the sample, pyroelectric probe and PMT on the same translation stage, it was ensured that the PMT is at the same distance from the sample throughout the scan. We also performed pump-probe experiments using 100 femtosecond laser pulses to obtain the temporal evolution of the nonlinear transmission.

## 4. RESULTS AND DISCUSSION

From the experiments it is found that the nonlinearity is essentially of the optical limiting type. Limiting shown by pure toluene is negligible, but the limiting efficiency increases substantially with the sample concentration. However, the PMT data (not shown) reveals that the scattering amplitudes for concentrated and dilute suspensions are rather similar. Thus induced scattering has only a limited contribution to the observed limiting, which, therefore, should have a strong non-thermal origin. Fig.2 shows the normalized transmission of the samples obtained at two different concentrations. Numerical fits show that the transmission T fits well to a three-photon absorption process, given by the equation [5]

$$T = \frac{(1-R)^2 \exp(-aL)}{\sqrt{p}\, p_0} \int_{-\infty}^{+\infty} \ln\left[\sqrt{1+ p_0^{\,2} \exp(-2t^2)} + p_0 \exp(-t^2)\right] dt \qquad (1)$$

where R is the reflectivity, L is the length, and $\alpha$ is the linear absorption coefficient of the sample. $p_0$ is given by $[2\gamma(1-R)^2 I_0^2 L_{eff}]^{1/2}$, where $I_0$ is the input intensity, $\gamma$ is the three-photon absorption coefficient, and $L_{eff} = [1-\exp(-2\alpha L)]/2\alpha$.

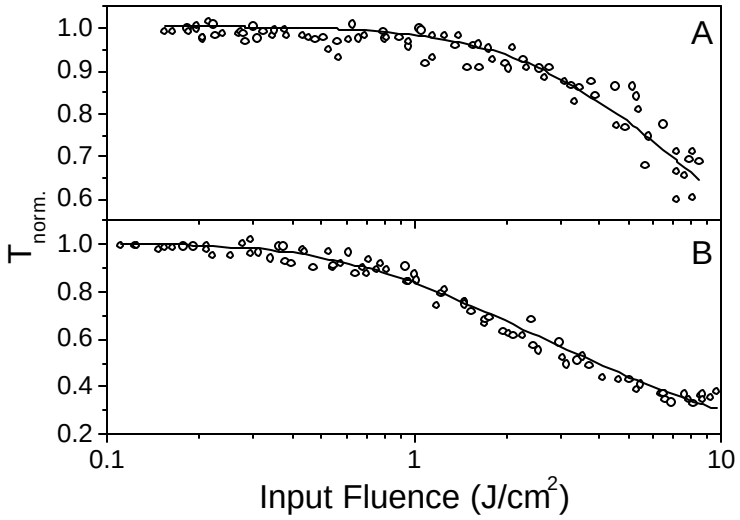


Fig. 2: Optical limiting in the samples. Linear transmissions are: A – 0.67; B – 0.19. Solid curves are numerical fits to a three-photon absorption process, given by equation 1.

The fact that the nonlinearity fits well to a three-photon process rather than to a two-photon process is interesting, since in the present case there are no compelling reasons for a fifth order nonlinearity to override the third order nonlinearity. However, a similar situation has been encountered in the case of semiconductors. For semiconductors, the optical nonlinearities in the transparent spectral region can be divided into two categories, namely, those due to bound electrons, and, those arising from the photo-excitation of free carriers. When the band gap becomes smaller than twice the pump photon energy, free carriers will be generated by a two-photon absorption process. If such free carriers start absorbing, then the net nonlinearity will appear as a fifth order one [6-8]. A similar photogeneration of free carriers and subsequent absorption have been speculated in metal nanoclusters also [9,10]. The situation is very similar here, and we believe that in the present case, two-photon induced interband transitions generate free carriers which subsequently absorb the pump radiation strongly, leaving the signature of a fifth order nonlinearity. Under this assumption a four-level system was modeled for these samples, and the corresponding rate equations have been solved, to estimate the nonlinear absorption cross sections. The two-photon cross section is calculated to be 1.9 x $10^{-44}$ $cm^4$ s, and the free carrier cross section to be 4 x $10^{-16}$ $cm^2$. The accuracy of these values is limited to their respective orders of magnitude, mainly because of the uncertainty in the values of level lifetimes used in the calculations.

To get some information on the temporal evolution of the limiting, we conducted femtosecond pump-probe experiments in pure toluene and the samples. 100 fs pulses at 400 nm were used for the measurements, in which the transmission of the probe pulse was monitored as a function of the probe delay. Typical results are shown in fig.3. A number of such measurements were made and the average lifetimes were calculated, assuming a single exponential growth function. While pure toluene has given a limiting lifetime of 501 ± 72 fs, the clusters give a lifetime of 1.45 ± 0.16 ps. This indicates that optical limiting in these materials is an ultrafast process.

## 5. CONCLUSIONS

Nanosecond laser excitation at 532 nm has revealed a fifth order nonlinearity in cluster molecules of Au in the size range of 29kDa Au, containing not more than 40 atoms. As the surface plasmon absorption band is absent in these clusters, plasmon bleach effects do not occur, and hence, the nonlinear absorption is completely of the optical limiting type. Induced thermal scattering is not prominent, and the origin of the nonlinearity appears to be two-photon absorption followed by free carrier absorption. The optical limiting lifetimes are found to be less than 2 picoseconds. Because of the above properties, these materials can be used as fast and efficient optical limiters.

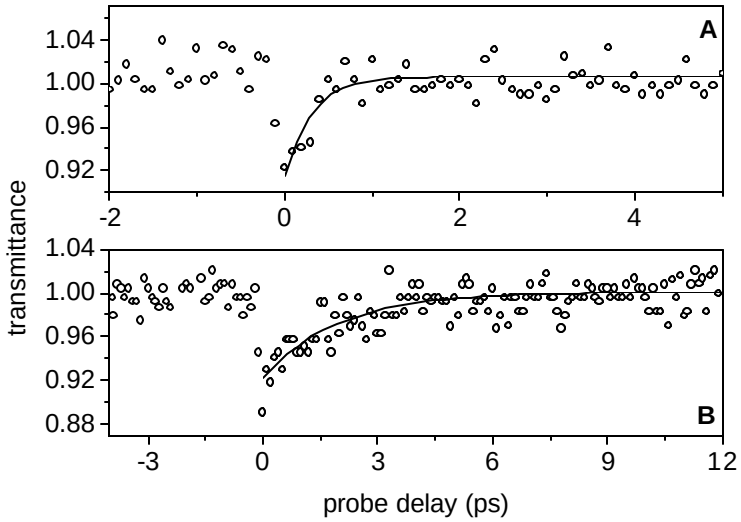


Fig 3: Typical graphs of the temporal evolution of optical limiting in (A) pure toluene and (B) the nanoclusters

## 6. ACKNOWLEDGEMENTS

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