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Long-Lived Charge-Separated States in Ligand-Stabilized Silver Clusters

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ABSTRACT: Recently developed synthesis methods allow for the production of atomically monodisperse clusters of silver atoms stabilized in solution by aromatic thiol ligands, which exhibit intense absorption peaks throughout the visible and near-IR spectral regions. Here we investigated the time-dependent optical properties of these clusters. We observed two kinetic processes following ultrafast laser excitation of any of the absorption peaks: a rapid decay, with a time constant of 1 ps or less, and a slow decay, with a time constant that can be longer than 300 ns. Both time constants decrease as the polarity of the solvent increases, indicating that the two processes correspond to the formation and recombination, respectively, of a charge-separated state. The long lifetime of this state and the broad optical absorption spectrum mean that the ligand-stabilized silver clusters are promising materials for solar energy harvesting.

Silver and gold nanoparticles with dimensions in the 10−100 nm range have optical properties that are dominated by plasmon resonances, which can be understood in terms of the properties of the bulk metals.[1] The optical properties of individual metal atoms, in contrast, are determined by discrete transitions between quantum-mechanical states. Understanding the transition from the quantum to the classical regime remains a central scientific challenge.[2] Small clusters, containing on the order of 10−100 metal atoms, are located at the mesoscopic boundary between the atomic/molecular regime and the bulk regime. They have been studied for several decades, either isolated in the gas phase or embedded in solid matrices, and have generally been found to exhibit molecule-like optical properties.[3]

More recently, solution-phase methods have been developed for the chemical synthesis of a variety of metal clusters with atomically precise structures, stabilized by thiolate ligands.[4] For small clusters, the number of ligands is comparable to the number of metal atoms; this means that the clusters are analogous to large organometallic molecules and have chemical, physical, and optical properties that are distinct from those of ligand-free gas-phase clusters. Understanding the size- and structure-dependent properties of these clusters would provide new insight into the transition from atoms to bulk materials and could lead to new principles for the development of materials for catalysis, energy conversion, and other applications.

Time-resolved optical spectroscopy is a powerful tool for gaining insight into the electronic states supported by clusters and into the transition rates between these states. Several transient-absorption experiments have been performed on Au clusters;[5] these experiments generally show a fast transient with a time constant that does not depend on pump power and lies in the range 0.3−2 ps. In many cases, the fast transient is followed by a much slower decay; most of the measurements did not resolve the slow kinetics, but there is one report of a decay time of 2.4 μs in 25-atom Au clusters.[6] Time-resolved luminescence measurements on 25-atom Au clusters with different ligands and different geometries also showed slow decay with time constants from 0.5−1.5 μs.[7,8] The fast transient can broadly be attributed to internal conversion, or relaxation between electronic energy levels within the cluster. The origin of the slower decay has been less clear, and systematic investigations have been complicated by the broad spectral features of the Au clusters.

We recently demonstrated the synthesis of monodisperse, ligand-stabilized silver clusters[9] with the general formula $(Ag_{44}SR_{30})^{4-}$.[10] These clusters exhibit a series of sharp absorption peaks throughout the visible and near-IR spectral regions; for this reason, we call them intensely broadband absorbing nanoparticles (IBANs). The unique optical absorption spectrum makes the IBANs ideally suited for transient-absorption measurements. Here we report the results of such measurements. As has been reported for Au clusters, we observed a fast transient followed by a much slower decay. The rates of these two processes are strongly correlated with the polarity of the solvent in which the clusters are dispersed. We therefore have identified the two processes as the formation and recombination of a charge-transfer state in the clusters.

IBANs were prepared and purified as previously reported.[9,10] Samples stabilized by 4-fluorothiophenol (4FTP) or 2-naphthalenethiol (2NPT) were prepared using *N*,*N*-dimethylformamide (DMF) as the solvent. In addition, samples stabilized by 4-mercaptobenzoic acid (4MBA) were prepared in water; methanol was added to this solution in order to improve its stability. 4MBA-stabilized samples were transferred into acetone or dichloromethane (DCM) using hexadecyltrimethylammonium bromide (CTAB) as a counterion transfer agent. The concentration of all samples was ~1.5 × 10^{-5} M.

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Figure 1a shows the linear absorption spectra of these samples. Discrete, molecule-like absorption peaks are seen throughout the visible and near-IR spectral ranges.[9] These peaks are broadened for samples in more polar solvents, but are otherwise largely insensitive to the choice of ligand or solvent. (The sample-dependent baseline is due to scattering in the solution.) This is quite unlike the plasmonic resonances that are observed for particles larger than 2 nm, which exhibit strong solvent-dependent shifts.[1]

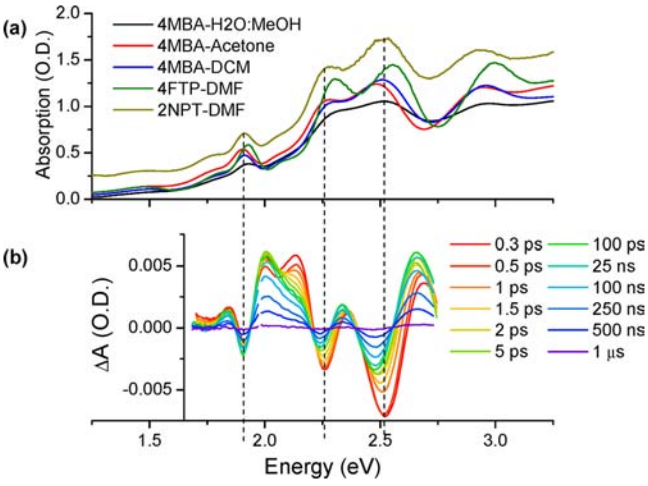

Figure 1. (a) Linear absorption spectra of 44-atom silver clusters stabilized with various thiolate ligands in various solvents. Labels refer to the ligands and the solvent; see the text for abbreviations. (b) Transient absorption spectra of 2NPT-stabilized silver clusters in DMF at various times after excitation by an ultrafast pump pulse at 2.98 eV.

We used transient-absorption spectroscopy to investigate in depth the optical response of the IBANs (using Ultrafast Systems HELIOS and EOS transient-absorption spectrometers). In these measurements, the sample was excited by an ultrafast pump laser pulse; after a certain time delay, a broadband probe pulse was passed through the sample, and the difference in probe transmission in the absence and in the presence of the pump was measured. The pump and probe pulses were derived from the output of a regeneratively amplified Ti:sapphire laser (Spectra-Physics Tsunami and SpitFire Pro). Most of the power from the amplified laser pulse was used to pump an optical parametric oscillator (Spectra-Physics TOPAS-C), which was used to produce tunable pump pulses. The pump beam was focused to a spot size of ~250 μm inside a cuvette containing the sample solution. The pump power was kept low enough to avoid damaging the sample, and the sample was rapidly stirred during measurements. For time delays shorter than 250 ps, the probe pulse was generated by focusing the remainder of the regenerative amplifier output into a sapphire crystal, and the pump−probe delay was controlled using a mechanical delay line. For time delays longer than 250 ps, the probe pulse was generated by an independent Nd:YAG laser focused into a photonic-crystal fiber, and the pump−probe delay was measured using a digital analyzer. Scattered pump light was subtracted from the measured spectra, and wavelength-dependent time delays were corrected for chirp in the probe pulse.

All of the IBAN samples described above show similar transient-absorption spectra; representative results are shown in Figure 1b. In all cases, bleach (reduced absorption) signals occur at all of the energies corresponding to peaks in the linear absorption spectra, and additional induced-absorption signals appear at well-defined energies between the bleach signals. These features are characteristic of state filling and excited-state absorption, respectively, in molecular systems. The simultaneous appearance of all the features clearly indicates that the spectral peaks all result from transitions within a single species, rather than reflecting a collection of different cluster types in the solution.

For all of the IBAN samples measured, the transient kinetics exhibit a fast transient with a time constant less than 2 ps and a slow decay with a time constant between 25 and 300 ns, similar to the fast and slow decays previously observed in Au clusters.[5,6] The fast transient is accompanied by a shift of the bleach features toward lower energies, away from the linear-absorption peak energies; the slow decay, in contrast, occurs uniformly at all energies, with no further shift in the spectral features (see Figure 1b). Quantitative evaluation of the kinetics was performed by global analysis of the transient spectra (using Ultrafast Systems Surface Xplorer Pro software). Principal spectral and kinetic components of the transient data were determined by singular value decomposition, and the principal kinetic components were fitted to a multiexponential decay convolved with a Gaussian instrument response function.[11] Only two time constants were required to describe all of the measured kinetics. This indicates that excitation is followed by rapid conversion into a single long-lived state, which slowly decays; there is no evidence for the involvement of additional intermediate states.

Larger metal nanoparticles also show a transient response on picosecond time scales due to the heating of conduction electrons and subsequent exchange of energy with the lattice.[1] The time scale of this response depends on the initial electron temperature and thus on the pump-laser power, with higher excitation power leading to slower decay. In the IBANs studied here, in contrast, the measured kinetics is independent of pump power. This provides additional evidence that the IBAN spectra reflect transitions between discrete, molecule-like states rather than plasmonic resonances.

The kinetics is also independent of the pump-photon energy when higher-energy peaks are excited, as illustrated by the representative data in Figure 2 and Table 1. In contrast, when the lowest-energy peak at 1.48 eV is excited, the fast transient is absent, while the slow decay remains unchanged; this indicates that 1.48 eV photons excite the clusters directly into the long-lived state. It is reasonable to believe that this state at 1.48 eV is the lowest-energy excited state in the system and that the fast transients for excitation at higher energies correspond to relaxation into this state. This interpretation is consistent with cyclic voltammetry data, which shows first oxidation and reduction peaks at approximately 0.2 and −1.1 V vs SHE, respectively, for 4MBA-stabilized IBANs in acetone.

It has been proposed that similar long-lived states in gold clusters may correspond to triplet electron configurations.[7] Triplet states generally can be deactivated by interaction with oxygen, so removing oxygen from the solution containing the clusters would be expected to increase the triplet lifetime. However, we found the slow decay in the silver clusters to be unaffected by removal of dissolved oxygen from the solvent through repeated freezing, pumping, and thawing.

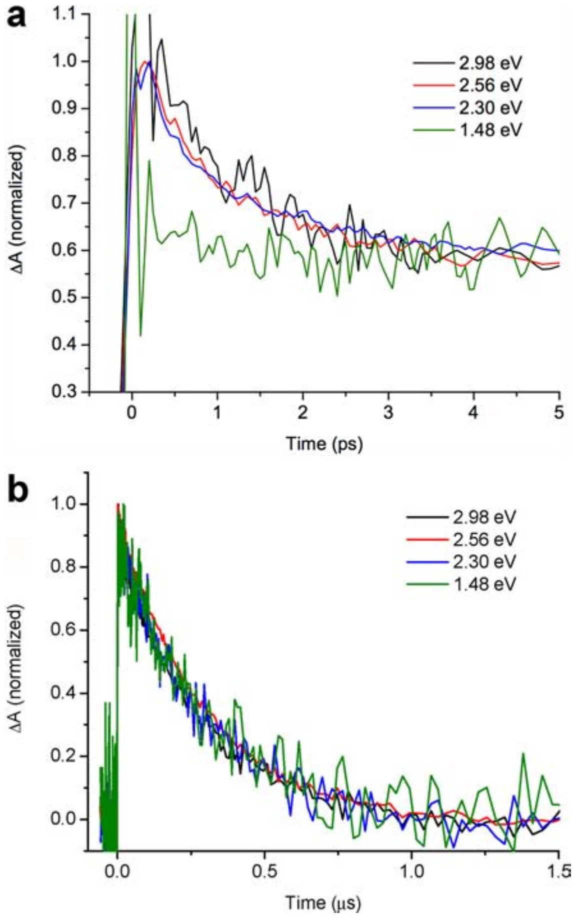

Figure 2. Transient-absorption kinetics for silver nanoclusters stabilized with 4FTP in DMF at a probe energy of 2.14 eV and different pump energies, as indicated; (a) and (b) show results for the same sample at different pump−probe delay times. The curves are normalized so that they all have the same values at long delay times.

Table 1. Time Constants of Transient Kinetics for Silver Clusters Stabilized with 2NPT in DMF

pump energy (eV)	τ_1 (ps)	τ_2 (ns)
2.98	1.03 ± 0.23	310 ± 1
2.56	1.15 ± 0.32	317 ± 7
2.30	1.02 ± 0.48	302 ± 9
1.48	0	314 ± 6

We can also rule out thermal effects as the cause of the slow decay: even if heating of the small clusters by the pump laser pulse caused a measurable change in their absorption, they would be expected to reach ambient temperature within less than 10 ps by exchanging heat with their surroundings.[12] Heating could be considered as a cause of the fast transient; in this case, though, any peak shifts would arise immediately after absorption of the pump pulse, and the peaks would shift back toward their unperturbed values as the clusters cooled back to ambient temperature. The experiments, in contrast, showed bleach features that shifted away from the linear-absorption peaks on picosecond time scales and remained at these lower-energy values throughout the slow decay (see Figure 1).

On the other hand, such a rapid and sustained red shift is consistent with a Stark shift induced by charge separation within the clusters. Efficient charge separation is also consistent with the very low luminescence quantum yield of these structures (~0.01%).[9] In addition, a low-energy charge-separated state is consistent with the broad, weak linear absorption around 1.48 eV in comparison with the higher-energy peaks.

Charge separation was previously suggested as a possible origin of long-lived states in gold clusters[7] but was considered to be unlikely on the basis of indirect spectroscopic evidence.[5g] On the other hand, the ligand dependence of fluorescence intensity from gold clusters was cited as evidence for the involvement of a ligand-to-metal charge transfer (LMCT) state.[8] As a more direct test of the possibility of charge transfer within the clusters, we compared the transient kinetics of the clusters in solvents with different polarity. To ensure a proper comparison, we compared only IBANs stabilized by 4MBA, which we were able to transfer into a range of different solvents.

The time constants of both the fast transient and the slow decay decrease significantly with increasing solvent polarity, as illustrated by the representative data in Figure 3 and Table 2. This is consistent with the Marcus theory of charge separation, with charge separation and recombination both occurring in the normal Marcus regime.[14] We note that the solvents with higher polarity also have stronger hydrogen bonding, which could also serve to increase the charge separation and recombination rates; while we cannot separate the two effects with the present

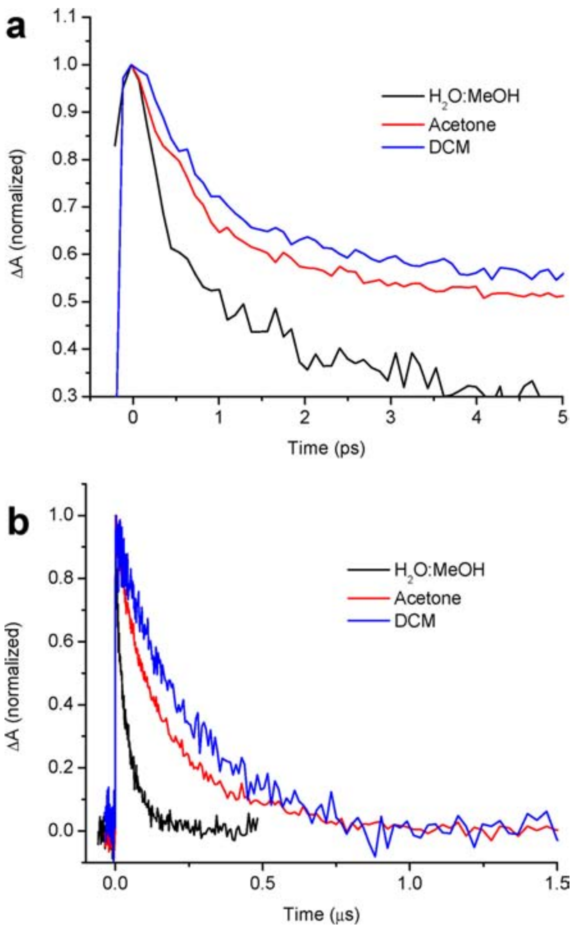

Figure 3. Transient-absorption kinetics for silver nanoclusters stabilized with 4FTP in different solvents at a pump energy of 2.30 eV and a probe energy of 2.14 eV; (a) and (b) show results for the same sample at different pump−probe delay times. The curves are normalized so that they all have the same initial values.

Table 2. Time Constants of Transient Kinetics for Silver Clusters with Different Ligands and in Solvents with Different Dielectric Constants ($\varepsilon_{\text{solvent}}$)

solvent	ligand	$\varepsilon_{\text{solvent}}$[a]	τ_1 (ps)	τ_2 (ns)
H_2O/MeOH	4MBA	67	0.24 ± 0.03	33 ± 1
acetone	4MBA	21	0.89 ± 0.08	148 ± 3
DCM	4MBA	8.9	0.96 ± 0.09	224 ± 6
DMF	2NPT	38	1.07 ± 0.21	311 ± 3
DMF	4FTP	38	1.1 ± 0.7	297 ± 2

[a] Data taken from ref 13.

experiments, both would support the interpretation that the long-lived state in the silver clusters is due to charge separation.

The strong sensitivity of the separation and recombination rates on solvent polarity indicates that there is a significant distance between the separated charges.[14] The reduction potentials of the isolated ligands are much lower than the measured reduction potentials of the clusters,[15] suggesting that the metal core acts as an acceptor and the ligands act as donors. Such an LMCT state[8] would be consistent with the results of electronic structure calculations for similar metal clusters, which predict occupied states located on the ligands that are 1−2 eV in energy below unoccupied states located on the metal cores.[9,16] We note that one must be careful when discussing "ligands" in these clusters. In gold clusters, a staple motif consisting of two SR ligands bridged by a single gold adatom has been identified, and it is known that larger clusters show oligomeric versions of this motif.[17] It is reasonable to expect that similar oligomeric units exist in these silver clusters; in this case, the units as a whole would act as the ligands and may be the electron acceptors.

In summary, transient spectroscopy has provided a clear demonstration that the peaks in the absorption spectrum of ligand-stabilized silver clusters correspond to transitions between discrete electronic states within the clusters. The transient kinetics involve a fast transient followed by a slow decay; the rates of these two processes are correlated with the solvent polarity, indicating that they correspond to charge separation and recombination within the ligand-stabilized cluster. The charge-separated state lies 1.48 eV above the ground state of the cluster and has a lifetime that varies from ~30 ns in polar solvents to ~300 ns in nonpolar solvents.

Although the current experiments demonstrate the existence of a charge-separated state, they do not identify its nature. A full understanding will require detailed knowledge of the atomic structure of the clusters.[18,19] It is most likely, though, that one of the separated charges is located on the ligands and the other on the metal core. This spatial separation, together with the long lifetime of the charge-separated state, should enable the separated charges to be extracted following photoexcitation. The clusters are therefore promising materials for photocatalysis, sensitization of electrochemical solar cells, and other solar-energy-harvesting applications, especially since they have such broad absorption spectra. The practical development of these applications will rely on advances in synthesis to improve the sample stability, particularly at room temperature and in aqueous solution.

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Notes

The authors declare no competing financial interest.

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