Optical Absorption of Gold Nanoparticles:
Origin and Effects of Silver Doping and Finite Temperature

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Gold nanoparticles have a number of important applications because of their unique optical properties. Large (> 5 nm diameter) gold nanoparticles exhibit a collective oscillation of the conduction electrons, called a surface plasmon resonance, when excited at appropriate wavelengths. In contrast, smaller thiolate-stabilized gold nanoparticles present very structured optical absorption spectra, and the connection between these two types of systems has not been well understood. Time-dependent density functional theory (TDDFT) calculations have recently been employed to elucidate the excitation spectrum of $Au_{25}(SR)_{18}^-$ and related nanoparticles. This particle can be interpreted as a "superatom", in which a core of essentially free electrons is surrounded by gold-thiolate oligomeric ligands. A charge-perturbed particle-in-a-sphere model has been developed to treat these systems, and this model can explain why the structured absorption spectra coalesce into a single plasmon resonance for larger nanoparticles.

Recently, experimental groups have introduced silver atoms into the $Au_{25}(SR)_{18}^-$ nanoparticle. In this work, the effect of silver doping is studied by investigating $Au_{25-n}Ag_n(SH)_{18}^-$ (n = 1, 2, 4, 6, 8, 10, 12) systems. Doping of the icosahedral shell of the metal core is energetically more favorable than doping of the metal-thiolate units or the center of the core. For $n \geq 2$, arrangements where the silver dopants are in close proximity tend to be slightly less favorable. However, energy differences are small and all conformations are accessible under experimental conditions. Boltzmann-averaged excitation spectra for these systems show similar features to the undoped $Au_{25}(SH)_{18}^-$. The main differences include a blue shift of the low-energy HOMO-LUMO peak and an increased intensity of the peak at 2.5 eV as the number of doping silver atoms increases. Silver doping lowers the energy of ligand-based orbitals and facilitates the transitions between the superatom orbitals. Silver-doped systems show broader excitation spectra due to a breaking of the symmetry of the superatom orbitals.

Previous theoretical work on absorption spectra of $Au_{25}(SR)_{18}^-$ and related nanoparticles has incorporated a broadening function in order to correlate TDDFT calculations (at 0K) with experimental spectra. In this work, density functional-based molecular dynamics simulations at 300K followed by TDDFT calculations at all points along the trajectories are performed to analyze the effects of finite temperature on the absorption spectrum.