Optical Properties of Bi-Icosahedral Au$_{25}$ and Au$_{24}$ Clusters: Influence of Central Gold Atom

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Abstract

Synthesis and characterization of bi-icosahedral Au$_{25}$ and Au$_{24}$ clusters

Results and discussion – Temperature-dependent optical absorption properties

Solvent effect on optical properties

Figure 6: Absorption maxima as a function of temperature for bi-Au$_{25}$ in Ethanol, 2 Butanol and 2,2,2-Trifluoroethanol. (A) comparison of low energy absorption in ethanol and toluene showing special influence of hydrogen bonding solvent. (B) low energy band as a function of temperature for hydrogen bonding solvent. (C) high energy absorption maximum as a function of temperature. Notice that the absence of wavy nature in high energy absorption maximum.

Figure 7: Luminescence decays of A) bi-Au$_{25}$ and Au$_{2}$ in Toluene, B) bi-Au$_{24}$ in two solvents. Note the increased decay time in ethanol showing the effect of hydrogen bonding on core-shell transitions.

Scheme 1. Carbon showing the hydrogen bonding influence on the low energy absorption

Conclusions

Absorption spectral features became sharper and the absorption maximum is shifted to higher energies for both the clusters with decrease in temperature.

Interesting solvent dependent absorption is observed for bi-Au$_{25}$ in ethanol when compared to toluene.

Combined measurements show that hydrogen bond of bi-Au$_{25}$ with ethanol is the reason behind this behavior.

Au$_{24}$ and Au$_{25}$ both can form H bonds but Au$_{25}$ rod is more stable than the Au$_{24}$ structure when it comes to H bond solvents.

The H bonding with coaxial C atoms cause the low energy absorption to swing around glass transition temperatures of the alcohols. Below the glass transition temperature, new optical features were observed.

Ultrafast luminescence measurements indicate the relaxation is similar for both clusters but temperature dependence has a dramatic influence on the relaxation.

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References

Figure 1: Crystal structures of bi-icosahedral Au$_{25}$ and Au$_{24}$ respectively

Our group studied the fundamental optical and electronic behavior of the quantum sized gold clusters to support the theoretical calculations. Earlier we studied bi-Au$_{24}$ and spherical Au$_{25}$ clusters and found that the core-shell electron plasmon and exciton phonon transitions are not as prominent as that of spherical Au$_{25}$ clusters. Akola and co-workers$^{[a,b,c]}$ performed molecular simulation for stability studies of these two clusters and found that there for an effect of central gold atom for the stability of the cluster. However, there is no systematic study delineating the electronic transitions in optical spectra of bi-Au$_{25}$ clusters and also will be interesting to probe if the clusters behave as molecules and show hydrogen bonding with solvents.

In this work, we carried out temperature dependent absorbance measurements and ultrafast luminescence measurements on these systems in order to study structural, electronic, and optical properties. To understand the effect of hydrogen bonding, measurements were carried out in alcoholic solvents such as ethanol, 2-butanol and 2,2,2-Trifluoroethanol, and compared with toluene.

Figure 2: Optical absorption spectra of bi-Au$_{25}$ and bi-Au$_{24}$ clusters. Note the absence of 670 nm peak that arises out of coupling of twoicosahedrons.

Figure 3: Absorption spectra at different temperatures for (A) bi-Au$_{25}$ and (B) bi-Au$_{24}$ in toluene. Both the clusters show similar behavior.

Temperature dependent absorption maximum vs. temperature for bi-Au$_{25}$ and bi-Au$_{24}$

Table 1: Energy gap vs. temperature and the strength of electronic-photon interactions from the analysis of bi-Au$_{25}$ and bi-Au$_{24}$ clusters.

Temperature (K) E$_g$(0) (eV) <h$\omega$> (meV) <C>

Figure 4: Temperature dependent absorption maximum vs. temperature for bi-Au$_{25}$ and bi-Au$_{24}$

Figure 5: Temperature dependent absorption of bi-Au$_{25}$ in Ethanol, 2-butanol and 2,2,2-Trifluoroethanol

Figure 6: Absorption maxima as a function of temperature for bi-Au$_{25}$ in Ethanol, 2 Butanol and 2,2,2-Trifluoroethanol. (A) comparison of low energy absorption in ethanol and toluene showing special influence of hydrogen bonding solvent. (B) low energy band as a function of temperature for hydrogen bonding solvent. (C) high energy absorption maximum as a function of temperature. Notice that the absence of wavy nature in high energy absorption maximum.

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