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

Over the past few years, atomically precise thiolate-protected quantum sized gold clusters of different sizes and shapes were synthesized and reported. These clusters have received vast research attention because of their exciting linear and non-linear optical, electrochemical, magnetic and catalytic properties due to quantized states of the confined electrons. 1-6 This quantum confinement leads metallic behavior of gold to nanoscale molecular behavior. Experimental and molecular simulation studies have been carried out to understand the fundamental theory behind the unique properties of the clusters and the cluster to nanoparticle transitions.

Starting from Brust-Stephens synthesis,8 properties of size and shape of thiol-gold prevails protected and stabilized gold clusters. However, with respect to other nanocusters only few phosphine-protected gold nanoclusters were studied during past decade. Tsukuda and co-workers10 synthesized the first Au$_n$(PPPh$_3$)$_{10}$(SC$_2$Ph)$_5$Cl$_2$ and Jin and co-workers11 synthesized the same cluster with different thiol ligand and later they synthesize bi-Au$_{25}$(PPPh$_3$)$_{10}$(SC$_2$Ph)$_5$Cl$_2$. Cluster-bi-icosahedral clusters are exciting because the majority of gold atoms are from the core shell-gold is minimum. Both bi-Au$_{25}$ and bi-Au$_{24}$ clusters are structurally similar except for the central gold atom in bi-Au$_{25}$ which is absent in bi-Au$_{24}$ cluster. (Figure 1)

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$_{25}$ and spherical Au$_{25}$ clusters and found that the core-shell-electronic properties and exciton phonon properties are not as prominent as that of spherical Au$_{25}$ clusters. 8 Aksela and co-workers9 performed molecular simulation for stability studies of these two clusters and found that there is an effect of central gold atom for the stability of the cluster. However, there is no systematic study delineating the bi-Au$_{25}$ in optical properties in the cluster and Au$_{24}$ 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 clusters in order to study structural, electronic, and optical properties. To understand the effect of hydrogen bonding, measurements were carried out in aliphatic solvents such as ethanol, 2-butanol and 2,2,2-Trifluoroethanol compared with toluene.

Results and discussion – Temperature-dependent optical absorption properties

- Absorption peaks become sharper and more pronounced features are observed with a decrease in temperature
- The energy maximum is shifted to higher energies with decrease in temperature

Table 1. Energy gap at 78 K and the strength of electronic interactions from the analysis of Au$_{25}$ and bi-Au$_{24}$ clusters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g(0)$ (eV)</th>
<th>$h\omega$ (meV)</th>
<th>$\langle C \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bi-Au$_{25}$ in toluene</td>
<td>2.24 ± 0.01</td>
<td>20 ± 10</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>bi-Au$_{24}$ in toluene</td>
<td>2.25 ± 0.01</td>
<td>20 ± 10</td>
<td>1.4 ± 0.2</td>
</tr>
</tbody>
</table>

Conclusions

- Absorption spectral features become 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.
- A$_{25}$ and A$_{24}$ both can form H bonds but Au$_{25}$ is more stable than the A$_{24}$ structure when it is linked to H bond solvents.
- The H bonding with coaxial C$_{2}$S atom cause the low energy absorption to swing around glass transition temperatures of the solvents. 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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Figure 6. Absorption maximum 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 specific influence of hydrogen-bonding solvent. (B) low energy band as a function of temperature in 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 A$_{25}$ in Toluene. B) bi-Au$_{25}$ in two solvents. Note the increased decay time in ethanol showing the effect of hydrogen bonding on core-shell transitions.

Figure 8. Absorption spectra of bi-Au$_{25}$ and bi-Au$_{24}$ clusters. Note the absence of 607 nm peak that arises out of coupling of two icosahedrons.