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

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Abstract

The thiol-gold molar ratio 2:1 combined with the Au$_{25}$ and Au$_{24}$ rods. The investigations are carried out on these two clusters as they are structurally similar except for the absence of central Au atom for bi-Au$_{24}$. The objectives of the work are to probe the influence of the central gold atom on the optical transitions and electron-phonon interactions in bi-icosahedral nanoclusters. The investigations are focused both on the electron-phonon as well as hydrogen bonding interactions of axial Cl atoms with hydrogen bonding solvents as these influence the optical transitions. It was theoretically shown that the absorption at 670 nm arises due to coupling of two icosahedral clusters which Au$_{25}$ and Au$_{24}$ does not. While for Au$_{25}$ broad band at ~950 nm was observed due to the interactions of the two units with Au$_{25}$ units, 415 nm shoulder and 383 nm band that is due to the electronic transitions in bi-Au$_{25}$ clusters. All these peaks becoming sharper and blue shifted when it goes to lower temperature and if increases the oscillator strength and also it showed a new peak around 480 nm in lower temperature. The electron-phonon interactions were obtained from fitting the band gap data as a function of temperature. Solvent dependent absorption measurements and ultraviolet-visible-light absorption measurements show the hydrogen bonding formation of clusters with alcoholic solvents.

Introduction

Over the last 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. This quantum confinement leads metallic behavior of gold to nonmetallic 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 & Schiffrin's synthetic, proper control of size and composition of the gold nano-particle precursors were synthesized and reported. However, with respect to other nanoclusters only few phosphine-protected gold nanoclusters were studied during past decade. Tsukada and co-workers synthesized the first Au$_{25}$ and Au$_{24}$ and Jin and co-workers synthesized the same cluster with different thiol ligand and later they synthesized bi-Au$_{25}$ and Au$_{24}$ and co-workers synthesized bi-Au$_{25}$ and Au$_{24}$ clusters. Bi-icosahedral nanoclusters are exciting because the majority of gold atoms are from the core shell while gold is minimum. Both bi-Au$_{25}$ and bi-Au$_{24}$ clusters are structurally similar except for the central gold atom in Au$_{25}$ which is absent in bi-Au$_{25}$ cluster. (Figure 1)

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$_{25}$ and spherical Au$_{24}$ clusters and found that the core-shell electron phonon and exciton phonon transitions are not as prominent that of spherical Au$_{24}$ clusters. Akola and co-workers 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$_{25}$ and bi-Au$_{24}$ properties and clusters 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 alcoholic solvents such as ethanol, 2-butanol and 2.2.2-Trifluoroethanol and compared with toluene.

Results and discussion – Temperature-dependent optical absorption properties

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 two icosahedrons.

![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 two icosahedrons.](image)

Absorption peaks become sharper and more pronounced features are observed with a decrease in temperature.

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.

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The energy maximum is shifted to higher energies with decrease in temperature.

Table 1. Energy gap variation and the strength of electron-phonon interactions from the analysis of bi-Au$_{25}$ and bi-Au$_{24}$ clusters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{g0}$ (eV)</th>
<th>$\Delta E$ (meV)</th>
<th>$\Delta C$ (meV)</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>

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

![Figure 4 - Temperature dependent absorption maximum vs. temperature for bi-Au$_{25}$ and bi-Au$_{24}$.](image)

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.
- Au$_{25}$ and Au$_{24}$ both can form H bonds but Au$_{24}$ rod is more stable than the Au$_{25}$ structure when it comes to H bond solvents.
- The H bonding with axial Cl atoms cause the low energy absorption to swing around glass transition temperatures of the alcohols. Below the glass transition temperature, no 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.

Acknowledgements

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Figure 6 - Absorption maximum as a function of temperature for (A) bi-Au$_{25}$ in EtOH, (B) bi-Au$_{25}$ 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 in hydrogen bonding and non hydrogen bonding solvents.

![Figure 6 - Absorption maximum as a function of temperature for (A) bi-Au$_{25}$ in EtOH, (B) bi-Au$_{25}$ 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 in hydrogen bonding and non hydrogen bonding solvents.](image)

Figure 7 - Luminescence decays of (A) bi-Au$_{25}$ and Au$_{25}$ 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 7 - Luminescence decays of (A) bi-Au$_{25}$ and Au$_{25}$ 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.](image)