Sensitive X-ray Absorption Near Edge Structure Analysis on the Bonding Properties of \( \text{Au}_{30}(\text{SR})_{18} \) Nanoclusters

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ABSTRACT: Au nanoclusters (NCs) with organothiolate protecting ligands are a field of great interest and X-ray absorption spectroscopy is a useful tool for the structure and property studies of these Au NCs. However, the Au NCs normally show broad and low-intensity features in the gold X-ray absorption near-edge structure (XANES) region, lowering the sensitivity of the technique and making it difficult to use for the analysis of Au NCs. In this work we report a sensitive gold L\(_3\)-edge XANES study on the bonding properties of the newly discovered \( \text{Au}_{30}(\text{SR})_{18} \) NCs utilizing a combined approach of the first derivative XANES spectra and quantum simulations. First derivative XANES spectra are compared with the well-studied \( \text{Au}_{25}(\text{SR})_{18} \) with the aim of determining the unique features of \( \text{Au}_{30}(\text{SR})_{18} \). It is found that the early XANES region of the Au NCs is significantly influenced by the gold–gold bonding environment in the surface sites, as the varying surface Au–Au bond lengths in \( \text{Au}_{25}(\text{SR})_{18} \) and \( \text{Au}_{30}(\text{SR})_{18} \) result in pronounced difference in the first derivative XANES. These findings can be consistently explained using site-selective quantum simulations of the XANES spectra based on the Au NC structural models. The XANES method presented in this work offers a useful tool for the sensitive analysis on structure and bonding properties of Au NCs.

1. INTRODUCTION

Ultra-small Au nanoclusters (NCs) protected with ligands have been an area of interest in the field of nanotechnology as they are an excellent candidate for a wide variety of potential applications, including catalysis,\(^1\) sensing,\(^2\) and bioimaging.\(^3,4\) A particular area of interest is Au NCs with protecting organothiolate ligands, due to their high stability and the ability for their size and number of atoms to be precisely controlled.\(^5–7\) One example of Au NCs with protecting organothiolate ligands is \( \text{Au}_{25}(\text{SR})_{18} \) (\( \text{Au}_{25} \) for short).\(^8\) \( \text{Au}_{25} \) has been well studied, providing information on its crystal structure,\(^9\) bonding properties,\(^10\) and electronic properties.\(^11\) As a result, \( \text{Au}_{25} \) serves as an excellent point of comparison for newly discovered Au NCs, as parameters and properties can be compared and contrasted with those of \( \text{Au}_{25} \).

The recently reported HCP-like \( \text{Au}_{30}(\text{SR})_{18} \) (\( \text{Au}_{30} \) for short) has been an area of interest as this is the first time in a thiolate-protected Au NC that this core geometry has been observed.\(^12–15\) Comparison with well-studied NCs such as \( \text{Au}_{25} \) could provide insight into the electronic and bonding properties present in \( \text{Au}_{30} \), which can in turn allow for this NC to be used in various applications in the future. Several techniques can be utilized to analyze NCs, including mass spectroscopy, which can provide information on the identity and number of atoms present in a NC, and X-ray crystallography, which can provide detailed information on the structure of a NC.\(^16,17\) X-ray crystallography can prove challenging, however, as high synthetic yield and purity are required for crystallography to be successful. Another powerful technique that will allow for the determination of these properties is X-ray absorption spectroscopy (XAS). In particular, XAS allows for X-ray absorption near edge structure (XANES) spectroscopy to be conducted, which can provide information on the electronic and bonding properties of the NC.\(^18\)

However, the Au-based XANES analysis has proved to be less useful than analysis of other elements because of the broad and weak features present in Au L\(_3\)-edge XANES data, which makes it difficult to differentiate between two NCs with a different structure.\(^19–21\) In this work a special technique is used based on the first derivative of XANES spectra. This improves the sensitivity allowing for the differences between the XANES spectra of two NCs to be clearly observed. To help support the experimental data, quantum simulations are used to generate theoretical XANES spectra using the known crystal structures of the NCs, resulting in a combined approach of experimental...
data and quantum simulations. To showcase this technique, Au30 is compared with Au25 using this more sensitive first derivative technique, which allows for subtle but significant differences between data sets to be more clearly observed. Through experimental data and theoretical simulations, the difference in bonding properties between Au30 and Au25 NCs is systematically studied from their core, surface, and staple sites to provide a better understanding of the properties of the recently discovered Au30 and to illustrate the usefulness of this more sensitive first derivative technique for XANES analysis.

2. RESULTS AND DISCUSSION

The total structures of Au25 and Au30 are shown in Figure 1a,d, respectively.9,12 To more clearly see the local structures, the staple sites are shown in Figure 1b,e, and core sites are shown in Figure 1c,f for Au25 and Au30, respectively. Note that "surface" Au atoms are also sometimes referred to as "vertex site of the kernel". It can be seen that both NCs have a similar staple-capping structure in the ligand shell, whereas the NC core geometry of the two clusters is very different (i.e., icosahedron for Au25 vs HCP for Au30).

In order to study the bonding properties of the NCs, the Au L3-edge XANES of Au25 and Au30 are compared in Figure 2a. A difference in the near-edge region of regular XANES can be barely observed between the two samples. To more clearly compare the differences of the XANES features, the first derivative XANES of the two NC samples is exhibited in Figure 2b. As shown in the figure, significantly improved sensitivity can be achieved in the comparison. Both NCs have a similar feature in the lower energy region which is labeled as feature A. A new feature around 13 eV from Au30 is observed and labeled as feature B. In order to understand the origin of these XANES features, experimental first derivative XANES is further studied by comparison with their site-specific XANES simulations.

In order to perform a reliable comparison between experimental and simulated first derivative XANES, the well-studied Au25 is tested in the simulation. In Figure 3a, the experimental data of Au25 are displayed together with the site-specific simulations from the surface, staple, and core sites. Feature A from the experimental data exhibits a match with those from the simulated surface and staple sites. These results prove that the simulation method is reliable. It is also noted that when the simulated first derivative XANES is calculated by the weight percentage, the simulation from the core site has almost no contribution because of the negligible amount of Au atoms.

Next, the experimental first derivative XANES from both NCs in association with their site-specific simulations are shown in Figure 3b. It is found that feature A from the experimental first derivative XANES in both of the NCs is contributed to by the surface and staple sites. The unique feature B from Au30 is significantly influenced by its surface site. Specifically, the simulated XANES from the surface site in Au30 shows a blue-shifted feature by comparing with the feature from Au25 ("blue-shifted" and "red-shifted" is used to describe the feature which is shifted at higher and lower energy, respectively). This blue-shifted feature in the simulation is consistent with feature B in experimental data from Au30. Therefore, features A and B in the experimental data from Au30 should correspond to the overlap of simulated XANES from its surface and staple sites. The important contribution from the surface site of Au30 leads to the unexpected feature B. Therefore, the results from Figure 3b indicate that the difference in experimental XANES is mainly influenced by the surface sites. Note that there is a small mismatch in the peak position between feature A of the Au30 experimental data and the simulation of the staple site. However, this mismatch does not influence the double-peak shape of the overall simulated XANES.

Figure 1. (a) Total structure of Au25, (b) staple-like motifs in Au25, (c) core structure of Au25, (d) total structure of Au30, (e) staple-like motifs in Au30, and (f) core structure of Au30 (yellow: central Au; purple: surface Au; blue: staple Au; red: sulfur).

Figure 2. Experimental Au L3-edge (a) XANES and (b) first derivative XANES of Au25 and Au30.
To understand how the difference in the Au−Au bond distance of surface sites in fluences the XANES, the bond distance distributions of representative surface sites of the NCs are plotted in Figure 4a,b. The corresponding local structural models of surface sites are also presented. Note that the entire bond distance distribution is reported, rather than an average value for that bonding environment. It is clear that the surface site from Au25 has considerably a longer averaged Au−Au bond distance than the surface site from Au30. In order to better understand the relationship between variation in the Au−Au bond distance and the location of peaks in the XANES spectrum, the lattice expansion test is performed on the simulated spectra. In this test, the simulated XANES from surface sites is compared with simulations using the expanded Au−Au bond distance, that is, all the bond distances are purposely expanded by 10% in the simulation. In Figure 4c,d, the simulations for both NCs exhibit a redshift when the Au−Au bond distance increases. Therefore, these simulation results prove that the blue-shifted first derivative XANES peak from Au30 (i.e., the feature B in Figure 2b) should be caused by the shorter Au−Au bond distance from the surface Au site. As mentioned previously, this peak mainly arises from the surface site, and so any variation in the Au−Au bond length involving the center or staple atoms should have no effect on the location of this peak.

3. CONCLUSIONS

In conclusion, X-ray absorption near-edge structure measurements in association with theoretical calculations probed the unique bonding properties of Au30 with comparison to Au25. It was found that the early region in the first derivative XANES spectra of the Au NCs is significantly influenced by the gold−gold bonding environment in NC surface sites. These findings can be consistently explained using quantum XANES simulations. This work demonstrates that HCP-like Au30 NCs have unique bonding properties differing from the
icosahedron-like Au_{25} NCs. The first derivative method was shown to have significantly improved sensitivity overall regular XANES on the structural and bonding analysis of Au NCs, and thus offers new opportunities toward more thoroughly understanding the structure-property relationships of many other Au NCs.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Au NCs. Au_{30} NCs were synthesized following a literature procedure. In the synthesis, 0.3 mmol of HAuCl_{3}·3H_{2}O and 0.348 mmol of TOAB were mixed together and dissolved in 15 mL of methanol in a 50 mL round-bottom flask at room temperature. The solution was stirred for 15 min, at which point the color was observed to change from yellow to a reddish orange. Next, 1.6 mmol of 1-adamantanethiol was added, changing the color to a light yellow. The solution was left for 15 min, and then 3 mmol of NaBH_{4} was added under vigorous stirring. After 1 week of stirring, a black precipitate containing Au NCs was isolated from the solution. The Au NCs were then washed with dichloromethane and extracted from the residue using benzene. The yield was determined to be approximately 20%. Au_{25} NCs were synthesized following a well-established literature procedure.

4.2. X-ray Absorption Spectroscopy. Au L_{3}-edge XAS measurements were collected in the transmission mode at the Sector 20-BM beamline of the Advanced Photon Source, located in Argonne National Laboratory in IL, U.S.A. Powder samples of the Au_{30} NC were packed into Kapton film pouches, sealed, and folded to ensure an adequate signal was obtained. A Au foil reference was measured simultaneously for calibration of the energy of Au L_{3} absorption edge. XAS data were collected at room temperature under normal conditions. XAS measurements of Au_{25} from previous work were used for comparison with the new measurements of the Au_{30} NC collected for this work.

4.3. Data Analysis. The simulated first derivative of XANES spectra in the three NCs were generated using the FEFF8.2 computer code. In the comparison between experimental first derivative XANES and site-specific simula-
tions, the simulated first derivative XANES of Au_{25} and Au_{30} was generated from the Au atoms in different surface, staple, and core sites based on the published total structures. One Au site contains the selected Au atom and its connected Au or S atoms. The types of Au sites are dependent on their bonding environment. In the analysis, only one Au atom in each type of Au site was selected and used in the simulation. Moreover, two surface and staple sites were found in Au_{30}. The other Au sites in the two NCs show a single type of bonding environment. Furthermore, the y-axis of simulated first derivative XANES was normalized by multiplying the value by weight percentage of each individual site (i.e., number of Au atoms in each site/total number of Au atoms).

The authors declare no competing financial interest.

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