Theoretical Investigation of Relaxation Dynamics in \( \text{Au}_{38}(\text{SH})_{24} \)
Thiolate-Protected Gold Nanoclusters

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Supporting Information

ABSTRACT: A subtle change in the electronic structure of thiolate-protected noble metal nanoparticles can result in distinctive energy relaxation dynamics. Corresponding investigations on different sizes and structures of thiolate-protected gold nanoclusters reveal their physical and chemical properties for further development of catalytic applications. In this work, we performed nonradiative relaxation dynamics simulations of the \( \text{Au}_{38}(\text{SH})_{24} \) nanocluster to describe electron-vibrational energy exchange. The core and higher excited states involving semiring motifs lying in the energy range of 0.00–2.01 eV are investigated using time-dependent density functional theory (TDDFT). The surface hopping method with decoherence correction combined with real-time TDDFT is used to assess the quantum dynamics. The \( \text{Au}_{23} \) core relaxations are found to occur in the range of 2.0–8.2 ps. The higher excited states that consist of core–semiring mixed or semiring states give ultrafast decay time constants in the range of 0.6–4.9 ps. Our calculations predict that the slowest individual state decay of \( \text{S}_1 \) or the slowest combined \( \text{S}_1 \sim \text{S}_{12}, \text{S}_1 \sim \text{S}_5 \sim \text{S}_6 \sim \text{S}_7, \) and \( \text{S}_1 \sim \text{S}_5 \sim \text{S}_9 \sim \text{S}_{10} \) decay involves intracore relaxations. The analysis of the phonon spectral densities and the ground state vibrational frequencies suggests that the low frequency (25 cm\(^{-1}\)) coherent phonon emission reported experimentally could be the bending of the bi-icosahedral \( \text{Au}_{23} \) core or the “fan blade twisting” mode of two icosahedral units.

INTRODUCTION

Advances in synthesis and isolation of thiolate-protected gold nanoparticles have led to developments in applications such as catalysis and photocatalysis.\(^1,\)\(^2\) Investigations of energy relaxation dynamics for different sizes and structures of thiolate-protected gold nanoclusters are needed to enable elucidation of the physical and chemical properties underlying these applications.\(^3,\)\(^4\) Quantum confinement effects become prominent for small gold nanoparticles less than 2 nm in diameter. Thus, the geometric structure of the system plays a role in its electronic structure,\(^5,\)\(^6\) and subtle changes in structure can lead to different electron dynamics.\(^7,\)\(^8\)\(^9\) Extensive experimental work has examined the electron relaxation dynamics of nanoclusters such as \( \text{Au}_{13}(\text{SR})_{13} \),\(^10\) and distinct time scales and relaxation mechanisms have been reported.\(^11,\)\(^12\) Recent theoretical electron-nuclear relaxation studies on the \( \text{Au}_{25}(\text{SH})_{18} \) nanocluster provided insights into the experimentally proposed relaxation mechanisms.\(^21,\)\(^24\) The study by Senanayake et al. showed that states arising from orbitals based on the semirings (i.e., the –SR–Au–SR– units surrounding the nanoparticle core) or other states are not observed at an energy lower than the core-based \( \text{S}_1 \) state.\(^24\) Moreover, it suggested that the experimentally observed time constants in the several picoseconds range could arise from core-to-core transitions rather than from a core-to-semiring transition. Recently, Jin and co-workers reported ultrafast relaxation dynamics of \( \text{Au}_{38}(\text{SC}_{2}\text{H}_{4}\text{Ph})_{24} \) nanoclusters and the effects of structural isomerism.\(^25\) This study found a correlation between the ultrafast relaxation dynamics and the geometric structures of two isomers of thiolate-protected \( \text{Au}_{38}(\text{SC}_{2}\text{H}_{4}\text{Ph})_{24} \). In another study, Knappenberger and co-workers reported low-frequency vibrations associated with the ligand shell of \( \text{Au}_{24}(\text{SC}_{2}\text{H}_{4})_{18} \) and \( \text{Au}_{38}(\text{SC}_{12}\text{H}_{25})_{24} \) nanoclusters that mediate the nonradiative relaxation dynamics.\(^26\) The reported modes include \( \text{Au}^{(1)}\sim\text{S} \) stretching (200 cm\(^{-1}\)) and \( \text{Au}(0)\sim\text{Au}(1) \) stretching (90 cm\(^{-1}\)) of the ligand shell.\(^26\)

The \( \text{Au}_{38}(\text{SR})_{24} \) nanocluster contains a face-fused bi-icosahedral \( \text{Au}_{23} \) core protected by six –SR–Au–SR– units surrounding the nanoparticle core.24

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SR—dimeric semirings and three −SR−Au−SR− monomeric semirings, forming a core-shell-like structure (Figure 1).27−29

![Figure 1. Geometry of the Au38(SH)24 nanocluster: side view and top view. (Au-gold, S-yellow, H-white).](image)

This nanocluster has attracted significant research interest in the areas of chirality, doping, and catalysis.26,30−34 In 2010, Aikens and co-workers28 showed that the arrangement of the semirings around the core yields an essentially D3-symmetric isomer for Au38(SR)24 compared to a higher energy C3 isomer. The electronic structure of the D3 isomer can be explained based on a particle-in-a-cylinder (PIC) model because of its nanorod-shaped gold core structure.28 Thus, the occupied and unoccupied orbitals near the HOMO−LUMO gap can be described by \( \Sigma, \Pi, \) and \( \Delta \) symmetries. The orbitals can be labeled as \( M_{\theta} \) where the azimuthal quantum number \( M = 0, 1, 2, \ldots \) corresponds to \( \Sigma, \Pi, \Delta, \ldots \) orbitals and \( l = 1, 2, 3, \ldots \) corresponds to the axial quantum number.28 The core−shell structure of the Au38(SR)24 nanocluster can result in interesting optical properties, but careful assignment of core and ligand contributions in optical properties is important. An ultrafast luminescence investigation proposed that the electron dynamics of Au38(SR)24 includes core-to-shell relaxations.25 However, a recent theoretical investigation on the luminescence origin of Au38(SR)24 suggested that the two lowest energy fluorescence bands arise predominantly because of a HOMO → LUMO transition that involves core-based orbitals.35

The experimental examination of ultrafast relaxation dynamics performed on the Au38(SC2H4Ph)24 nanocluster suggests that the isomer with a bi-icosahedral Au38 inner core shows rapid decay (1.5 ps) among excited states followed by nanosecond relaxation to the ground state (GS), and that a higher energy structural isomer exhibits similar relaxation processes.35 The femtosecond experiments were performed on the Au38(SR)24 isomer pumped at 490 nm/1050 nm and probed in the visible range (0.0−2.3 eV). A two-state relaxation model similar to a mechanism proposed for [Au32(SR)18]−1 was proposed. The picosecond relaxations in both isomers were assigned to core−shell charge transfer or to electronic rearrangement within the metal core.35 The authors suggested that the picosecond decay in Au38(SR)24 could be an electronic rearrangement within the metal core based on previous experimental and theoretical work on other thiolate-protected gold clusters.11,12,36 For the Au38(SR)24 isomer with a bi-icosahedral core, they also reported a coherent phonon emission at 25 cm−1 with pumping in the near-infrared region.25

Overall, further experimental and theoretical work is required to fully understand the nonradiative relaxation dynamics of the Au38(SR)24 nanocluster. Herein, the focus of this theoretical study is to reveal the electron-nuclear dynamics and give insights into the relaxation mechanism of the thiolate-protected Au38(SR)24 nanoparticle. In this study, we use the lowest energy D3 isomer of the Au38(SH)24 nanocluster for the relaxation dynamics calculations.

## COMPUTATIONAL METHODOLOGY

We have performed ab initio real-time nonadiabatic molecular dynamics (NA-MD) simulations to study the NA dynamics in the Au38(SH)24 nanocluster. The fewest switches surface hopping (FSSH)37 algorithm with the classical path approximation and a time-dependent Kohn−Sham (FSSH−TDKS) description of electronic states38 was used in our calculations. The reported geometrical and electronic structural changes (~0.05 Å) in the Au38(SH)24 nanocluster core25 are smaller than the reported geometrical and electronic structural changes (~0.33 Å) in the [Au32(SR)18]−1 nanocluster upon photo-excitation.39 Therefore, the classical path approximation in the NA-MD calculation approach is expected to be suitable to describe the nonradiative relaxation dynamics of the Au38(SH)24 nanocluster. The decoherence-induced surface hopping (DISH)39 scheme is utilized to include decoherence effects. The FSSH simulations in this work are performed using the PYXAIMD program.40,41

The methodology used here is similar to our previous work on [Au32(SR)18]−1.25 The Au38(SH)24 nanocluster geometry optimization is performed at the PBE42/TZP (frozen core) level of theory in the Amsterdam Density Functional (ADF) software package to obtain the relaxed geometry at 0 K. The PBE/TZP level of theory was used to keep the calculations consistent with our previous investigation on [Au32(SR)18]−1.24

The zero-order regular approximation44 is used to treat scalar relativistic effects in gold. Linear response time-dependent density functional theory (TDDFT) calculations were performed using the same level of theory to compute the electronic excitations and the relevant absorption spectrum of Au38(SR)24. Absorption spectra were convoluted with Gaussian functions with full width at half-maximum values of 0.2 eV and 40 nm for the spectra plotted in electronvolt and nanometer, respectively. A GS vibrational frequency calculation was performed using ADF at the same level of theory to obtain the vibrational modes of the cluster. The ADF GUI was used to plot the orbitals.

The 0 K system was thermalized through a temperature ramping calculation performed at 300 K. After the temperature ramping, MD simulations were performed through DFT calculations in the Vienna Ab initio Simulation Package (VASP).45 We used projector-augmented wave pseudopotentials,36 a kinetic energy cutoff value of 402.0 eV for the temperature ramping calculation and a 301.8 eV energy cutoff value for the MD and NA coupling calculations, a 24 Å simulation box size, gamma points, and the PBE functional in all of our VASP calculations. A MD trajectory of 5 ps in length was computed with a 1 fs integration time step. The NA coupling elements were calculated following the same approach we used for the [Au32(SH)18]−1 system.24

The FSSH calculations employ 3.5 ps length sub-trajectories starting from 10 different initial geometries. For each NA-MD trajectory, 1000 realizations of the stochastic FSSH/DISH state hopping trajectories were considered. We used 100 realizations of the stochastic FSSH/DISH state hopping trajectories for the largest calculation with ninety-eight excited states to reduce the computational cost.
The important electronic excited states contributing to the optical absorption spectrum of Au$_{38}$(SH)$_{24}$ in the energy range of 0.00–2.01 eV (visible range) were analyzed. The excited-state population decay times and the GS population increase times were calculated for the Au$_{38}$(SH)$_{24}$ nanocluster using the same equations and procedure mentioned in our previous study. The phonon spectral density plots were drawn with a resolution of 4.8 cm$^{-1}$.

**RESULTS AND DISCUSSION**

The experimental optical absorption spectrum for the Au$_{38}$(SR)$_{24}$ nanocluster displays low energy peaks that lie around 0.9, 1.2, 1.7, and 2.0 eV. The Au$_{38}$(SH)$_{24}$ spectrum calculated at the PBE level of theory gives similar peaks at 0.99, 1.26, 1.74, and 2.01 eV, as shown in Figure 2, which is in good agreement with the experimental spectrum from ref 47. The calculated spectral peak positions are also in agreement with the PBE/DZ frozen core optical absorption spectrum of the Au$_{38}$(SR)$_{24}$ nanocluster displaying low energy peaks that lie around 0.9, 1.2, 1.7, and 2.0 eV.47 The Au$_{38}$(SH)$_{24}$ spectrum was used to define the excited states that will be used in the FSSH–TDKS calculations.

Table 1 shows the excitations with the highest oscillator strengths up to 1.5 eV and their respective transitions with the highest weights for the two allowed excited state symmetries A$_2$ and E (these are the dipole-allowed excited-state symmetries as they contain the totally symmetric representation upon taking direct products with the dipole moment operator). The most significant transitions responsible for a particular excitation were identified based on their weights, which are all above 0.9 for the lowest energy excited states of Au$_{38}$(SH)$_{24}$. The excitations around 1.15–1.29 eV primarily arise from transitions out of the HOMO−LUMO gap (Figure 3) and transitions out of HOMO−4 to LUMO/LUMO + 1 (Π$_1$→Π$_2$) and transitions out of HOMO − 4 to LUMO/LUMO + 1 (Π$_1$→Π$_2$). However, for the 1.29 eV peak, the Σ$_3$→Π$_1$ transition has a small contribution to the oscillator strength, whereas the Π$_1$→Π$_3$ transitions have higher contributions to the oscillator strength because of their higher weights. The Π$_1$→Π$_3$ transition would be forbidden for a perfectly cylindrical system. Similar observations have been made by Aikens and co-workers.

The first absorption peak (0.99 eV) arises primarily because of a Π$_2$→Π$_1$ transition that has the highest oscillator strength and weight (Table 1), which is in agreement with previous results. In Figure 3, the degenerate orbitals are labeled as two different orbitals. For example, HOMO and HOMO − 1 are exactly degenerate in the 0 K PBE/TZP optimized structure but become nondegenerate as the nanocluster vibrates and distorts from its equilibrium structure during the NA-MD calculations. The labeling leads to two excited states that originate primarily from HOMO and HOMO − 1 to LUMO and LUMO + 1 for the 0.99 eV peak in Table 1. This labeling was used to define the excited states that will be used in the FSSH–TDKS calculations.

The phonon spectral density plots were drawn with a resolution of 4.8 cm$^{-1}$.

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**Figure 2.** Calculated PBE/TZP optical absorption spectrum for Au$_{38}$(SH)$_{24}$. Inset: Absorption spectrum in wavelength (nanometer).

**Figure 3.** PBE/TZP orbitals near the HOMO−LUMO gap and their relative energies (in electronvolt) for Au$_{38}$(SH)$_{24}$.
include the Slater determinants present in the TDDFT calculations.

Figure 4 demonstrates the variation of the orbital energies with time for the Au$_{38}$(SH)$_{24}$ cluster as obtained from the MD simulations. The orbital energy variation shows the near-degenerate nature of several sets of the orbitals. For example, the HOMO and HOMO − 1 as well as the LUMO and LUMO + 1 are nearly degenerate. As mentioned above, the degeneracies of the orbitals shown in Figure 3 were obtained by performing a single-point calculation on the relaxed geometry at 0 K. However, the MD simulation was performed at 300 K. During the dynamics, the Au$_{38}$(SH)$_{24}$ cluster geometry can have distortions in the x, y, and z directions that break the perfect $D_3$ symmetry of the optimized Au$_{38}$(SH)$_{24}$ geometry. During the MD simulation, the HOMO–LUMO gap of the Au$_{38}$(SH)$_{24}$ cluster is approximately 0.70 eV (Figure 4), which is smaller than the 0.83 eV gap obtained at 0 K.

Relaxation Dynamics of the Low Energy Excited States ~1.5 eV. First, we performed relaxation dynamics only on the $S_1$, $S_2$, $S_3$, and $S_4$ states (which correspond to $\Pi_2$ → $\Pi_3$ transitions) as a test case both with and without an energy correction to the excited states. The HOMO–LUMO gap for Au$_{38}$(SH)$_{24}$ is ~0.7 eV during the MD simulation, which is ~0.15 eV less than the experimental optical gap of ~0.9 eV reported elsewhere. Therefore, a 0.15 eV energy correction is added to the excited states to analyze how the relaxation dynamics will differ with the additional energy correction. Adding an energy correction only lengthens the GS growth times (by 16–30%), while the decay time constants are less affected. Overall, the time constants and the relaxation trends of these states do not change significantly with the added correction (see the Supporting Information, Figure S1 and Table S1). Therefore, in this section, the excited-state population relaxation dynamics calculations for all twenty-five states (Table 2) will be discussed without the correction added. The relaxation dynamics of these twenty-five states will
provide insights about the core state (∼1.5 eV) relaxations in the Au38(SH)24 nanocluster.

The GS growth times and decay times were then calculated for states S1−S25 (Table S2). In the presence of all twenty-five states, the population evolutions of the S1, S2, S6, and S7 states (Figure 5) follow similar relaxation patterns to the case in which only the S1, S2, S6, and S7 states were considered (Figure S1).

For all twenty-five excited states, the GS growth times are in the range of 6.4−207 ps. The GS growth times are relatively short except when states S15, S19, S20, S24, and S25 are excited. The overall growth times are 1−2 orders of magnitude shorter than the growth times of [Au25(SH)18]−1,24 which suggests that the identity of the thiolate-protected nanocluster is a critical factor for tuning the lifetimes of the excited electrons.

The S11 state (HOMO−2 → LUMO) gives the slowest decay time constant (∼8.2 ps) when its population is fit to an exponential. However, this S11 state population has a nonexponential decay after 2 ps because of population transfer to S12 (HOMO − 2 → LUMO + 1) (Figure 6a). Hops to higher excited states are allowed in the FSSH approach depending on the calculated probability for the hop and whether the kinetic energy of the system is able to accommodate the increase in electronic energy.38 The S12 population mainly transfers back to the S11 state (Figure 6b). For this reason, fitting the nonexponential S11 population decay to an exponential may not result in an accurate decay constant. At 3.5 ps, the S11 state retains 57% of its initial excited-state population (Figure 6a). Because of fast population exchange between S11 and S12, fitting the total population of S11 and S12 to one exponential could give a better idea about the decay (Figure 6c). The decay constant calculated for the combined S11 and S12 state population is 9.7 ps. At 3.5 ps, the combined S11 and S12 states retain 67% of the initial excited-state population of S11.

The fitting of the combined population of two or more states to an exponential is expected to be reasonable because several states would be probed by the same pump/probe pulse experimentally, and the observed decay will need to factor in more than one state. Therefore, we calculated decay time constants for several other combined state populations. At this point, the core states were grouped based on the orbitals involved and possible population transfers between the states. For example, S1, S2, S6, and S7 originate from the HOMO/HOMO − 1 → LUMO/LUMO + 1 transitions where the

Figure 5. Evolution of excited-state populations starting in (a) S1, (b) S2, (c) S6, and (d) S7 excited state.

Figure 6. (a) Evolution of excited-state populations starting in S11. (b) Evolution of excited-state populations starting in S12. (c) Evolution of the total population of the S11 and S12 states when S11 is excited. Populations of other states up to S25 are not shown for clarity.
HOMO and HOMO – 1 as well as the LUMO and LUMO + 1 are nearly degenerate. Thus, the population of S1 can easily be transferred to S2, S6, and S (Figure 5a). The total population of S1, S2, S6, and S10 was fit to an exponential when the S1, S2, S6, and S10 states were excited separately. Similarly, the other core states were grouped and their combined population decays were calculated (see the Supporting Information, Table S3). The S1, S2, S6, and S10 total population when the S6 state was excited and the S6, S9, and S10 total population when the S6 and S10 states were excited gave slower population decay compared to their individual decay constants. The combined S1−S−S−S−S state population decays are in the range of 6.4–10.1 ps and the combined S1−S−S−S−S state population decays are in the range of 4.1–10.7 ps. These decay time constants are similar to the combined S1−S12 population decay time of 9.7 ps.

At this point, it is difficult to compare our decay time constants directly with the experimentally observed time constants. The experimental time constants have been observed by using two pump frequencies (490 nm/1050 nm) and a range of probe frequencies. In our calculations, we look at each state relaxation separately rather than pumping the nanocluster system with a specific frequency. The individual state decay constants calculated for Au38(SR)24 in our study are in the range of 2.0–8.2 ps, whereas the combined state population decay constants are in the range of 2.0–10.7 ps. They agree with the picosecond time scale observed experimentally. Our calculations show that the slowest decays (the individual decay of S11 or the slowest combined S11−S12, S1−S−S−S−S, and S1−S−S−S−S= decays) involve HOMO → 2 → LUMO/LUMO + 1, HOMO/HOMO → 1 → LUMO/LUMO + 1, and HOMO/HOMO → 1 → LUMO + 3/LUMO + 4 transitions, which are intracore relaxations (Figure 3).

Relaxation Dynamics of the Higher Excited States up to ~2.01 eV. Jin and co-workers have proposed that the fastest 1.5 ps decay observed experimentally could arise from a core–shell relaxation or an intracore relaxation in the lowest energy Au38 isomer.25 They used a probe pulse with the energy covering ∼0.90–2.33 eV (530–1300 nm) in their experiments.26 In this section, we analyze the relaxation dynamics of the excited states lying beyond the energy of 1.5 eV in the Au38(SH)24 nanocluster optical absorption spectrum (Figure 2). The relaxation dynamics of the excited states lying above 1.50 eV is potentially important to understand the involvement of the semiring states because the 0.00–1.50 eV energy range only covers the gold core states. Here, we have considered the significant excitations appearing in the 0.00–2.01 eV energy range in Figure 2.

There are several notable excitations in the energy range of 1.70–2.01 eV (Table S4). Among them, the excitation around 1.74 eV has a relatively strong oscillator strength value (0.0549) that mainly originates from transitions out of HOMO → 2/HOMO → 7 orbitals to LUMO/LUMO + 1 orbitals (semiring → Π+) and from the transition out of HOMO → 2 to LUMO + 2 (Σ1 → Σ0). HOMO → 6 and HOMO – 7 are semiring orbitals, whereas HOMO – 6 and LUMO + 2 are gold core-based orbitals. The transition dipole moment components from the Σ1 → Σ0 transition are large, even though the weight of this transition is smaller than some of the others. Thus, the 1.74 eV peak is a combination of excitations involving both the gold core and semirings, where the Σ1 → Σ0 transition yields the main contribution because of its high transition dipole moment. The notable excitations around 1.85–2.01 eV have mixed transitions from orbitals involving both the gold core and semirings. However, the strongest excitation at 2.01 eV (oscillator strength of 0.1021) is mainly composed from the semiring (HOMO – 12/HOMO – 13) → LUMO transitions. Comparable findings have been observed by Aikens and co-workers at the PBE/DZ level of theory for Au38(SR)24.28

Therefore, we considered orbitals ranging from HOMO-13 to LUMO + 6 to define the single excitations for the FSSH–TDFS calculations (Tables 2 and S5). The decay times of the excited-state population were calculated for all ninety-eight states (Table S6). In the presence of the higher excited states, the relaxation trend of the S1–S25 states is preserved. The S11 population transfers its population into the S12 state, although by a lesser amount (Figure 2a). Thus, fitting its population decrease to an exponential may suffer a less significant error compared to the case involving only twenty-five states. The S12 population primarily transfers back to the S11 (Figure 2b).

Fitting the S11 (HOMO – 2 → LUMO) population to an exponential gives a slower decay time constant of 7.6 ps. After 3.5 ps, the S11 state retains 58% of its initial excited-state population (Figure 2a). Fitting the total population of the S11 and S12 states to an exponential gives a time constant of 8.8 ps. At 3.5 ps, the combined S11–S12 state population retains 66% of the initial S11 population (Figure 2c). The combined state population decay for the core states was calculated again in the presence of higher states. The S1, S6, S10, and S12 total population when S6 is excited and the S9, S10, and S10 total population when S6 and S10 are excited gave slow population decay in the range of 9.7–10.8 ps, which is similar to the case where only the core states were present.

The higher energy states S26–S28 have decay time constants in the range of 1.4–4.9 ps. The rest of the higher states (S40–S98) have much shorter time constants in the range of 0.6–1.7 ps. The S40–S98 states are mainly composed of transitions out of the semiring-based orbitals. In general, the decay times of higher energy states are shorter because of the higher density of states at these energies.

The semiring states mainly arise out of d orbitals from gold atoms and p orbitals from sulfur atoms. Thus, replacing the H ligands with the experimentally used ligands may not affect excited-state energies and their decay times significantly. Slight shifts in energies are possible as different ligands display different electron donating/withdrawing capabilities, although previous work59,60 on Au25(SR)18 has shown that these ligands similarly shift both the HOMO and LUMO and have relatively small effects on excited-state energies.

Electron–Phonon Interactions in the Au38(SH)24 Cluster. Vibrations in the Au38(SH)24 nanocluster can lead to nonradiative relaxation of excited states. Therefore, it is important to understand which nuclear vibrational motions couple most strongly with electronic states to understand the dynamics of electronic relaxations in these systems.

In this section, we present the phonon spectral densities obtained for core states (S1–S15) that demonstrate the vibrational modes that are correlated with the nonradiative relaxations (i.e., relevant electron–phonon interactions). The phonon spectral density plots were obtained by taking Fourier transforms of the normalized autocorrelation function of the energy gap fluctuation for a pair of electronic excited states of interest. The pair of electronic excited states could be the GS and an electronic excited state or two different electronic excited states. The analysis of the phonon spectral densities
showed intense peaks around 24.2, 33.9, 48.4, and 53.2 cm$^{-1}$ for Au$_{38}$(SR)$_{24}$ when only the core states (up to $\sim$1.5 eV) were considered in the relaxation dynamics (Figure S3). Among the prominent peaks, the peak around 24.2 cm$^{-1}$ was found to be the highest in intensity. This peak at 24.2 cm$^{-1}$ was observed when the spectral densities are plotted considering the energy gap fluctuation between the GS-S$_{15}$, GS-S$_{18}$, and GS-S$_{23}$ (Figure 7). The S$_{15}$ excited state arises from the transition out of HOMO$^{-2}$ to LUMO$^{+4}$. The S$_{18}$ and S$_{23}$ states arise from the transitions out of HOMO$^{-3}$ and HOMO$^{-4}$ to LUMO$^{+2}$, respectively.

To correlate the observed vibrational frequencies to the Au$_{38}$(SR)$_{24}$ cluster geometry, we compared the phonon modes obtained by the NA-MD calculation to the GS frequency calculation performed with ADF. The ADF frequency calculation gave several interesting vibrational modes arising from the gold core as well as from semiring motifs. A clear “bending mode” of the bi-icosahedral Au$_{23}$ core at its interior 3-fold face was observed at a very low frequency of 23.5 cm$^{-1}$ and a “fan blade twisting” of two icosahedral units was also observed at 25.9 cm$^{-1}$ (Figure 8). Several other core, semiring, and mixed core–semiring vibrational modes were observed in the low frequency range of 27.4–43.5 cm$^{-1}$. Gold core vibrations were noted in the range of 43.5–49.2 cm$^{-1}$ including a core breathing mode around 45.1 cm$^{-1}$. Frequencies in the range of 90.4–96.3 cm$^{-1}$ correspond to semiring bending vibrations. Other prominent gold core vibrations are present at a higher frequency of 104.7 cm$^{-1}$ and in the range of 121.1–148.3 cm$^{-1}$. Vibrational modes found in the range of 219.5–293.6 cm$^{-1}$ are primarily the Au(core)–S and Au(I)–S stretching modes.

It is possible that the intense frequency in the phonon spectral density that we observe around 24.2 cm$^{-1}$ from NA-MD calculations is the bending of the bi-icosahedral Au$_{23}$ core or the “fan blade twisting” of two icosahedral units (Figure 8), which could largely lead to nonradiative relaxation of the Au$_{38}$(SH)$_{24}$ nanocluster. Similarly, the low frequency coherent phonon emission reported at 25 cm$^{-1}$ by Jin and co-workers$^{25}$ could also be the bending of the bi-icosahedral Au$_{23}$ core or the “fan blade twisting” mode of two icosahedral units. In addition, there is a very small vibrational mode around 106.5 cm$^{-1}$ in Figure 7d which could be the gold core breathing vibration appearing around 104.7 cm$^{-1}$ in the ADF frequency calculation.

**CONCLUSIONS**

TDDFT and a time-dependent Kohn–Sham description of electron-vibrational dynamics (FSSH–TDKS) have been used to investigate the nonradiative relaxations in the Au$_{38}$(SH)$_{24}$ nanocluster. The orbital energy variation during the MD simulation indicated a loss of exact degeneracies in orbitals due
to geometrical distortions in the cluster during the dynamics. 

\text{Au}_{19}(\text{SH})_{14} \text{ has a small HOMO–LUMO gap during the MD simulation which is } \sim 0.7 \text{ eV. The relaxation dynamics performed on the } S_1, S_2, S_6 \text{ and } S_{10} \text{ states both with and without an energy correction of 0.15 eV showed that the correction lengthens the GS growth times only by 16–30\%.}

The GS growth times and excited state decay times were calculated for excited states up to \sim 1.5 eV which covers the Au_{12} core states \text{ ( } S_1, S_{12} \text{). The GS growth times upon excitation of the } S_{11}, S_{12} \text{ states were found to be in the range of } 6.4–207 \text{ ps, which are } 1–2 \text{ orders of magnitude shorter than the growth times reported for the } [\text{Au}_{14}(\text{SH})_{13}]^- \text{−1 nanocluster. Relaxation out of the } S_{11} \text{ state (HOMO } – 2 \text{ } \rightarrow \text{ LUMO) gives the slowest decay time constant (\sim 8.2 ps). Population transfer was observed between } S_1 \text{ and } S_{12}. \text{ Fitting the total population of the } S_{11} \text{ and } S_{12} \text{ to an exponential gave relatively slow decay time constants in the range of } 9.6–10.7 \text{ ps, which is similar to that for the initially excited } S_1 \text{ state. The slowest state decays involve intracore relaxations.}

Relaxation dynamics of the higher excited states covering up to \sim 2.01 eV involve relaxations coming from the core, mixed core–semiring, and semiring states \text{ ( } S_1, S_{98} \text{). The relaxation trends of the } S_1–S_{12} \text{ states were preserved in the presence of all ninety-eight states. Fitting the } S_{11} \text{ (HOMO } – 2 \text{ } \rightarrow \text{ LUMO) population to an exponential gave a relatively slow decay time constant of 7.6 ps. Fitting the total population of } S_{11} \text{ and } S_{12} \text{ to an exponential gave a time constant of 8.8 ps. The } S_{9}, S_{10} \text{ and } S_{10} \text{ excited-state decays gave slow combined time constants in the range of } 9.7–10.8 \text{ ps. Higher excited states } S_{89}–S_{89} \text{ have decay time constants in the range of } 1.4–4.9 \text{ ps. The } S_{89}–S_{98} \text{ states, which consist of transitions out of the semiring orbitals, have shorter time constants in the range of } 0.6–1.7 \text{ ps.}

Nonradiative relaxation of the Au_{14}(SH)_{14} excited states are driven by nanocluster vibrations. The analysis of the phonon intraspectral densities showed peaks around 24.2, 33.9, 48.4, and 53.2 cm\(^{-1}\) from the NA-MD calculations. The ADF GS frequency calculation gave several interesting vibrational modes arising from the gold core as well as from semiring motifs. Among them, the low-frequency “bending mode” of the bi-icosahedral Au_{14} core at 23.5 cm\(^{-1}\) and the “fan blade twisting” mode of two icosahedral units observed at 25.9 cm\(^{-1}\) were prominent. One or both of these vibrational modes could have shorter time constants in the range of 0.6–1.7 ps.

Comparison of excited-state lifetimes with and without the energy correction, ground-state population increase lifetimes and excited-state population decay lifetimes for the first 25 states and for higher excited states, transitions involved in the excited states from 1.50 to 2.01 eV, and Fourier transforms of autocorrelations functions of fluctuations of the energy gaps (PDF)

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\text{Notes}

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