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Coherent Vibrational Dynamics of $[\text{Au}_{25}(\text{SR})_{18}]^-$ Nanoclusters†

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Coherent vibrational dynamics can be observed in atomically precise gold nanoclusters using femtosecond time-resolved pump-probe spectroscopy. It can not only reveal the coupling between electrons and vibrations, but also reflect the mechanical and electronic properties of metal nanoclusters, which holds potential applications in biological sensing and mass detection. Here, we investigated the coherent vibrational dynamics of $[\text{Au}_{25}(\text{SR})_{18}]^-$ nanoclusters by ultrafast spectroscopy and revealed the origins of these coherent vibrations by analyzing their frequency, phase and probe wavelength distributions. Strong coherent oscillations with frequency of $40 \text{ cm}^{-1}$ and $80 \text{ cm}^{-1}$ can be reproduced in the excited state dynamics of $[\text{Au}_{25}(\text{SR})_{18}]^-$, which should originate from acoustic vibrations of the $\text{Au}_{13}$ metal core. Phase analysis on the oscillations indicates that the $80 \text{ cm}^{-1}$ mode should arise from the frequency modulation of the electronic states while the $40 \text{ cm}^{-1}$ mode should originate from the amplitude modulation of the dynamic spectrum. Moreover, it is found that the vibration frequencies of $[\text{Au}_{25}(\text{SR})_{18}]^-$ obtained in pump-probe measurements are independent of the surface ligands so that they are intrinsic properties of the metal core. These results are of great value to understand the electron-vibration coupling of metal nanoclusters.

Key words: Atomically precise gold nanoclusters, Electron-vibration coupling, Acoustic vibration, Femtosecond transient absorption

I. INTRODUCTION

The coupling between nuclear vibrations and electrons (electron-vibration coupling) in nanostructures has significant impact on their photophysical properties [1–4]. The strength of electron-vibration coupling and the vibration frequencies can determine the photo-excited state relaxation pathways and time constants of nanocrystals, which are important for their applications in photon energy storage and conversion [5, 6]. Electron-vibration coupling of metal nanoparticles and quantum confinement systems have been investigated by both experimental methods and theoretical simulations [7–10]. Both longitudinal optical vibrations and acoustic vibrations have been reported for different types of nanocrystals [8, 11–13]. In experiment, the following three techniques have been used to probe the electron-vibration coupling: low temperature absorption or emission spectroscopy that can resolve the vibronic peaks [14–16], resonant Raman scattering spectroscopy [17, 18], ultrafast pump-probe spectroscopy that can probe the coherent vibrational dynamics [8, 19–21]. It was reported that the time domain and frequency domain methods are complement-
terary, that is, frequency domain (Raman spectroscopy) measurements are more suitable for high frequency detection while time domain measurements (ultrafast spectroscopy) are good at low frequency measurements [1, 22]. Moreover, it requires samples with high monodispersity and less surface defect for ideal electron-vibration coupling investigations.

Atomically precise gold nanoclusters (NCs) bridge the metallic nanoparticles (NPs) and small complexes, which have no surface defects and well-defined compositions and crystal structures [23]. Small gold NCs possess discrete energy levels and excitonic absorption peaks, which are similar to small molecules [24]. These unique features make gold NCs an ideal model to understand the electron-vibration coupling of nanostructures. Many efforts have been made to understand the exciton dynamics and electron-vibration coupling in gold NCs [24–26]. Low temperature absorption spectroscopy study on Au$_{25}$(SR)$_{18}$ (SR stands for thiolate ligands) NCs showed that both acoustic vibration of the metal core (around 180 cm$^{-1}$) and optical vibration (around 350 cm$^{-1}$) of the surface structures can couple to electrons [14, 16]. Terahertz Raman spectra on Au$_{n}$ NCs revealed an acoustic breathing mode of the metal core at around 123 cm$^{-1}$ [17]. Coherent vibrations have been observed as oscillations in the transient absorption kinetics for several different sized Au NCs protected by different groups [27–30]. These coherent vibrations may have potential applications in biological sensing and mass detection [31]. Nevertheless, several questions regarding the coherent vibrations in Au NCs remain controversial: (i) what is the origin of these coherent oscillations? (ii) how these vibrations affect the exciton dynamics? (iii) what is the surface environment effect? Answering these questions calls for careful time-resolved experiments and detailed analysis on the TA dynamics of Au NCs.

Here, we use the femtosecond transient absorption (TA) spectroscopy to probe and analyze the coherent vibrational dynamics of atomically precise [Au$_{25}$(SR)$_{18}$]$^{-}\ $NCs. With near band gap excitation (1.55 eV), coherent oscillations with frequency of 40 cm$^{-1}$ and 80 cm$^{-1}$ can be observed. It is found that the coherent vibration around 80 cm$^{-1}$ show higher intensity and they damp quickly within the first three periods. Data analysis indicates that the 40 cm$^{-1}$ oscillations show similar phase at all probe wavelengths while the 80 cm$^{-1}$ oscillations exhibit significant phase shift on two sides of ground-state bleaching (GSB) maximum around 670 nm. Such an observation indicates that the 80 cm$^{-1}$ mode originates from the frequency modulation of the excited states while the 40 cm$^{-1}$ mode arises from the amplitude modulation of the spectrum. The phase of the oscillations at the starting time indicates that both two vibrational modes arise from the displace excitation mechanism. Moreover, Au$_{25}$ NCs show ligand-independent coherent vibrational dynamics, which reflects little influence of the surface capping ligands on the acoustic vibration.

II. EXPERIMENTS

A. Sample preparation

The preparation of [Au$_{25}$(SR)$_{18}$]$^{-}\ $NCs protected by three types of ligands (HSG: glutathione, PET: phenylethanethiolate, and HS:Nap: 1-naphthalenethiolate) followed the procedures reported in a previous study [32]. The nanocluster samples were kept in fridge at 4 °C before the femtosecond experiments.

B. Steady state and transient absorption spectroscopy

The UV-Vis absorption spectra were performed on a Shimadzu UV-3600plus spectrometer. The transient absorption spectroscopy measurements were performed on a commercial Ti:Sapphire amplified laser system which has been described elsewhere [33]. The UV-Vis absorption spectra of Au$_{25}$ NCs remained the same before and after the femtosecond transient absorption spectroscopy. Both the steady state and transient absorption measurements were performed in toluene for [Au$_{25}$(PET)$_{18}$]$^{-}\ $and [Au$_{25}$(SNap)$_{18}$]$^{-}\ $NCs and in water for [Au$_{25}$(SG)$_{18}$]$^{-}\ $NCs.

III. RESULTS AND DISCUSSION

FIG. 1 shows the electronic absorption spectra of [Au$_{25}$(SR)$_{18}$]$^{-}\ $ (Au$_{25}$ for short) and the crystal structure (inset). The structure of Au$_{25}$ consists of an Au$_{13}$ metal core and six Au$_{2}$(SR)$_{3}$ staple-like motifs. The lowest absorption band is split into two peaks around 670 nm and 800 nm, which is ascribed to the strong spin-orbital coupling effect [34]. The absorption peak between 600 nm and 700 nm experiences red-shift from [Au$_{25}$(SG)$_{18}$]$^{-}\ $ to [Au$_{25}$(SNap)$_{18}$]$^{-}\ $, which agrees with the results in the previous work [32]. Previous
work on the coherent vibrational dynamics of CdSe quantum dots reported that excitation to higher excited states would weaken the coherent vibration intensity [8]. Moreover, theoretical work by Nomura and Kobayashi suggested similar excitation dependent coupling strength [35]. Therefore, we looked into the TA spectrum pumped at 800 nm (1.55 eV), which is slightly above the HOMO-LUMO gap (1.3 eV) of the Au25 NCs.

FIG. 2 shows the TA data map of [Au25(SR)18]− pumped at 800 nm and probed in the visible region. The red color represents positive excited state absorptions (ESA) while the blue color stands for negative ground-state bleaching. In the initial 5 picoseconds (ps for short), one can observe significant coherent vibrations at almost all probe wavelengths (FIG. 2(A)). Fast Fourier transform gives two frequencies of 2.4 THz (80 cm−1) and 1.2 THz (40 cm−1) (FIG. 2(C, D)), which agrees well with a previous study on the same nanocluster [36]. It is found that the 80 cm−1 mode dominates the probe range between 600 nm and 750 nm and that the 40 cm−1 mode is more significant in the probe range between 450 nm and 600 nm. According to the previous studies [29, 36, 37], the low frequency oscillations (lower than 100 cm−1 in frequency) observed in the TA coherent oscillations should arise from the acoustic vibrations of the Au13 core. Except the amplitude and frequency, phase and damping time are also important parameters for the oscillation dynamics of nanostructures because they can reflect the starting time of the vibration and the mechanical properties of the systems, respectively [38]. To obtain the damping time and phase information, we fitted the coherent oscillation dynamics at selected wavelengths using a damped cosine function superimposed on the electronic relaxation:

$$\Delta A = e^{-t^2/2\sigma^2} \cdot \left[ A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} \cos(\omega t + \varphi) \right]$$  \hspace{1cm} (1)$$

where $\sigma$ is the pulse width of the laser, $\tau_1$ and $\tau_2$ represent the electronic relaxation lifetimes, $\tau_3$ is the damping time of the oscillation, $\omega$ and $\varphi$ are the frequency and phase of the oscillations, respectively.

As shown in FIG. 2(B), the TA kinetics probed around 490 nm and 640 nm can be well fitted by Eq.(1). One can observe that both the two modes damped quickly within three periods. The damping time constants of the coherent oscillations probed at 490 nm and 640 nm were fitted to be 2.8 ps and 1.7 ps respectively. The fast damping of coherent vibrations has been widely observed in Au NCs with different sizes, and it is found that the damping could be dependent on both the intrinsic properties of the metal nanoparticles and the surrounding environment [4, 31]. Previous study on the coherent vibrational dynamics on gold nanoparticles reported that surface capping molecules played a minor role in the damping of oscillations [31]. In very small gold nanoclusters, on the other hand, surface capping molecules should play more important roles in both electronic and mechanical properties. It was reported that the coherent vibrations in Au25 could assist the electronic relaxation [29], which could lead to the rapid damping in oscillations. Furthermore, the same study reported that the coherent oscillations were independent of the surface ligands and surrounding solvents [29], which ruled out the environmental effect.

After a closer look at the phase of these oscillations, it is found that the two modes with frequency of 40 cm−1 and 80 cm−1 exhibit different behaviors. The TA kinetics probed between 450 nm and 600 nm show in-phase oscillation around 40 cm−1, while the oscillations (80 cm−1) probed on two sides of the ground-state bleaching around 670 nm show a phase shift of $\pi$ (FIG. 3). The phase indicates the starting time of the oscillation, which can also reveal the origin of these oscillations. When the wave-packet modulates the excited state energy via electron-vibration coupling, the
FIG. 2 (A) TA data map of $[\text{Au}_{25}(\text{PET})_{18}]^-$ with 800 nm (1.55 eV) excitation, (B) TA kinetic traces showing the coherent oscillations and the corresponding fits. Fast Fourier transform results of the coherent vibrational dynamics of $[\text{Au}_{25}(\text{PET})_{18}]^-$ probed at (C) 630 nm and (D) 550 nm after subtraction of the population dynamics. One can observe that coherent vibrations probed at 630 nm show both 1.2 THz and 2.4 THz modes, while that probed at 550 nm only exhibits 1.2 THz mode.

FIG. 3 (A) TA spectra probed at selected time delays, the black arrow indicates the position where phase shift occurs, (B) TA kinetic traces probed at selected wavelengths.

The frequency of the electronic transition would be modified, which would lead to a phase shift of oscillation on two sides of an absorption band [8]. On the other hand, it was reported that the transition moment (or amplitude of electronic transition) can also be modulated by electron-vibration coupling via non-Condon effect. As a result, one would observe in-phase oscillations with electronic transition amplitude modulated by coherent vibrations.

We further analyzed the peak position of the ground-state bleaching around 670 nm by comparing the TA spectra at different time delays (FIG. 4(A)). One could...
observe that ground-state bleaching peak position experiences periodic shift and the period is estimated to be around 0.4 ps, which agrees with the 80 cm$^{-1}$ mode. Considering that the coherent oscillations on two sides of the ground-state bleaching show a phase shift of $\pi$, we can determine that the vibration around 80 cm$^{-1}$ should originate from the frequency modulation (FIG. 4(B)), which modulates the energy levels and the absorption frequency. On the other hand, the excited state absorption and the ground-state bleaching between 430 nm and 620 nm (FIG. 4(C)) do not exhibit significant shift. Instead, only the peak intensity shows periodic modulation at different time delays with frequency of 40 cm$^{-1}$. Such an observation also agrees with the fact that the TA dynamics in this probe range shows in-phase oscillations. Therefore, the vibration around 40 cm$^{-1}$ should arise from the amplitude modulation, which modulates the absorption amplitude (FIG. 4(D)). It is worth noting that both two mechanisms (phase and amplitude modulations) could contribute to the two modes observed in Au$_{25}$, phase analysis could indicate the dominant contribution of each mechanism.

The phase can reflect the starting time of the oscillations, which can also explain the origin of the oscillations [38]. Different mechanism may initiate the coherent vibrations in metal nanoclusters and other nanostructures. The mechanism of coherent oscillation generation can be determined from the initial phase of the oscillations. If the coherent oscillations show a sine type wave, it should arise from the impulsive excitation, in which the launching time of the oscillations is much shorter than the period [39, 40]. On the other hand, if the oscillations show a cosine type wave, it should originate from the displacive excitation, in which the initiation of the oscillations is comparable to the period of the oscillations [41, 42]. Here, both two modes (40 cm$^{-1}$ and 80 cm$^{-1}$) of Au$_{25}$ exhibit cosine type waves. Therefore, displacive excitation mechanism should account for the coherent oscillation generation in Au$_{25}$ NCs, which agrees with the previous study on gold NCs. In this mechanism, photo-excitation will induce nuclear motion by changing the equilibrium position of the nanoclusters in the excited state.

Finally, we probed the effect of surface protecting ligands on the coherent vibrations of Au$_{25}$ NCs. We compared the TA dynamics of Au$_{25}$ NCs protected by three kinds of surface ligands: HSG: glutathione, PET: phenylethanolthiolate, and

FIG. 4 (A) TA spectra (ground-state bleaching around 670 nm) at different time delays, the inset shows the probed time in the coherent oscillations (80 cm$^{-1}$ mode), (B) schematic diagram showing the mechanism of frequency modulation, (C) TA spectra (ESA band probed between 435 nm and 620 nm) at different time delays, the inset shows the probed time in the coherent oscillations (40 cm$^{-1}$ mode), (D) schematic diagram showing the mechanism of amplitude modulation.
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FIG. 5 TA data map of (A) $[\text{Au}_{25}(\text{SG})_{18}]^-$ and (B) $[\text{Au}_{25}(\text{SNap})_{18}]^-$ nanoclusters with 780 nm excitation (1.6 eV).

FIG. 6 (A) TA spectra probed at 3 ps of three $\text{Au}_{25}$ NCs protected by different surface ligands. (B) TA kinetic traces probed at around 650 nm of three different $\text{Au}_{25}$ NCs. (C) FFT results on the coherent vibrational dynamics probed at 650 nm for three $\text{Au}_{25}$ NCs after subtraction of the population dynamics.

HSNap: 1-naphthalenethiolate. The TA spectra of $[\text{Au}_{25}(\text{SG})_{18}]^-$ and $[\text{Au}_{25}(\text{SNap})_{18}]^-$ are shown in FIG 5, and the ground-state bleaching in TA spectra around 700 nm is slightly redshifted from $[\text{Au}_{25}(\text{SG})_{18}]^-$ to $[\text{Au}_{25}(\text{PET})_{18}]^-$ and $[\text{Au}_{25}(\text{SNap})_{18}]^-$ (FIG. 6(A)), which agrees with the trend in their steady state absorption. With excitation energy near their $E_g$, all three $\text{Au}_{25}$ NCs show significant coherent oscillations in their TA dynamics (FIG. 6(B)). Coherent vibrations around 80 cm$^{-1}$ show similar intensity, frequency and lifetimes (FIG. 6(B, C)). The mass loading effect of the coherent vibrations was predicted in gold NCs by theoretical calculations [32]. Here, by comparing three different $\text{Au}_{25}$ NCs, we found little influence of the surface ligands on the vibration frequency. Moreover, coherent oscillations in all three $\text{Au}_{25}$ nanoclusters were damped quickly in three periods (FIG. 6(B)). Since fast damping was reproduced in three $\text{Au}_{25}$ NCs with different surface capping ligands, the rapid damping of coherent vibrations in $\text{Au}_{25}$ should be intrinsic properties of the metal core in NCs.

IV. CONCLUSION

In summary, we have probed and analyzed the coherent vibrational dynamics of $\text{Au}_{25}$ by femtosecond pump-probe spectroscopy. Strong coherent oscillations around 40 cm$^{-1}$ and 80 cm$^{-1}$ can be observed in $[\text{Au}_{25}(\text{PET})_{18}]^-$ NCs after near band gap excitation. Phase analysis on the coherent oscillations indicates that the 40 cm$^{-1}$ and 80 cm$^{-1}$ vibrational modes should arise from the amplitude and frequency modulation of the electronic transition, respectively. The cosine type waves of oscillations of both two modes suggest that displacive mechanism should be the origin of coherent vibration generation in $\text{Au}_{25}$. Moreover, little surface ligands effect was found in the coherent vibrational dynamics of $\text{Au}_{25}$ NCs. All these results are of great value.

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to understand the electron-vibration coupling in metal NCs.

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