

Review

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Deep-nanometer-scale terahertz spectroscopy using a transistor geometry with metal nanogap electrodes

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Abstract

Terahertz (THz) spectroscopy is a powerful tool for characterizing electronic properties and vibronic excitations in various types of solids, liquids, and gases, and it has been extensively used not only for basic science but also for industrial applications. Recently, it has become necessary to understand electronic and vibronic excitations at the nanometer (nm) scale to realize state-of-the-art quantum nanodevices and the synthesis of new molecules for medicine. However, it is challenging to perform THz spectroscopy at the nm scale because the diffraction limit of electromagnetic waves hinders tight focusing of THz radiation at the nm scale. Here, we introduce a novel technique for THz spectroscopy using metal nanogap electrodes. Metal nanogap electrodes integrated with a THz antenna are employed to capture sensing targets, such as a single semiconductor quantum dot (QD) or molecule. Even extremely weak THz absorption can be detected with high sensitivity by measuring the THz-induced photocurrent through the sensing target. Taking advantage of THz-induced photocurrent spectroscopy, the electronic structures in single QDs as well as the vibrational states in single molecules are systematically investigated. The present characterization technology for nm-scale systems provides a key scientific foundation for creating nanodevices with new functions.

Introduction

Measurement technology is crucial for manufacturing. Terahertz (THz) electromagnetic waves¹, which lie between the microwave and infrared (IR) spectral ranges, have great potential in manufacturing processes for the characterization of material and electronic properties. Compared with visible/IR radiation, THz electromagnetic waves are less affected by scattering owing to their long

wavelengths and can deeply penetrate materials, which is beneficial for imaging^{2–5} and spectroscopy^{6–9} applications. Furthermore, THz electromagnetic waves have small photon energies (1 THz = ~4 meV); therefore, they are non-ionizing and biologically safe. Among their advantages, we emphasize that THz photon energies match various energy/frequency scales (quantization energies, plasma frequencies, etc.) in nanomaterials, such as quantum dots (QDs)^{10,11}, carbon nanotubes (CNTs)^{12,13}, and nanowires (NWs)^{14,15}, allowing THz electromagnetic waves can interact with various types of electronic excitations. Furthermore, molecular vibration frequencies, such as center-of-mass motions, bending modes, and rotational modes, lie in the THz range. Such features make THz spectroscopy an attractive and powerful tool for

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characterizing the properties of various types of nanomaterials and molecules. These features of THz spectroscopy are complementary to IR spectroscopy, which is often used to study interatomic vibrations in molecules.

However, the long wavelengths of THz electromagnetic waves pose challenges for performing spectroscopy at the nanometer (nm) scale. The typical wavelengths of THz waves lie between 3 mm and 10 μm (corresponding to 0.1–30 THz). Because of the diffraction limit, it is difficult to focus THz electromagnetic waves on nm-scale samples. Therefore, conventional THz measurements using free-space optics, such as THz time-domain spectroscopy^{8,16} and Fourier transform IR spectroscopy^{10,11}, have mainly been performed on samples several millimeters in size², as schematically shown in Fig. 1a. This is acceptable for the measurement of large samples, such as semiconductor wafers and biological tissues^{16–19}. However, with the progress in nanotechnology, the demand for measuring the properties of single nanostructures is increasing. For instance, to realize advanced quantum nanodevices for information processing, the electronic structures and dynamic properties of single quantum nanostructures must be understood, and advanced pharmaceutical applications require the characterization of molecules at the individual level. Therefore, while THz spectroscopy at the nm scale is becoming increasingly necessary, it is far beyond the capability of conventional THz spectroscopy techniques.

Over the last decade, several groups have attempted to overcome the diffraction limit by building on-chip systems with integrated THz sources, waveguides, and detectors^{20–25}. Compared with conventional free-space measurement systems, on-chip THz spectroscopy systems can reduce the sample size to the subwavelength range, and the necessary sample volume is significantly reduced to approximately the cubic micrometer level, as schematically shown in Fig. 1b. Furthermore, an on-chip THz

spectroscopy system can be integrated with microfluidic structures^{26–28}. THz metamaterial resonators^{29–32} can also be introduced to compress the mode volume and improve the signal-to-noise ratio. Femtomolar-order sensitivity has been reported^{29,30} for the detection of large biomolecules, such as deoxyribonucleic acid (DNA). However, the sensitivities of such systems remain insufficient for measuring the THz spectra of single nanostructures. To realize nm-scale THz spectroscopy, new measurement schemes that are different from simple transmission or reflection measurements are required.

Nanoscale THz spectroscopy is very challenging because it requires a new scheme not only for focusing THz electromagnetic waves onto nm-scale regions but also for high-sensitivity detection of the extremely weak absorption by nm-scale systems. Three types of nanoscale THz spectroscopy techniques have been reported, namely, THz scattering-type scanning near-field optical microscopy (THz s-SNOM)^{33–38}, THz scanning tunneling microscopy (THz-STM)^{39–48}, and THz single-electron tunneling spectroscopy (THz-SETS)^{49–54}. In these measurements, the THz electromagnetic wave is focused onto nm-scale systems using either a scanning probe or nanogap electrodes, as schematically shown in Fig. 1c. By detecting THz electromagnetic waves scattered by a measurement target or by measuring the photocurrent induced by THz photoexcitation in the sample, the THz response of single quantum nanostructures can be detected. By providing a key scientific basis for understanding the physics and the application of nanostructures and single molecules, nm-scale THz spectroscopy has great potential in the fields of nanoscience and technology.

This paper aims to provide a comprehensive review of the recent progress in nm-scale THz spectroscopy using THz-SETS. In Section 1, we provide a general introduction to conventional and nm-scale THz spectroscopy. Section 2

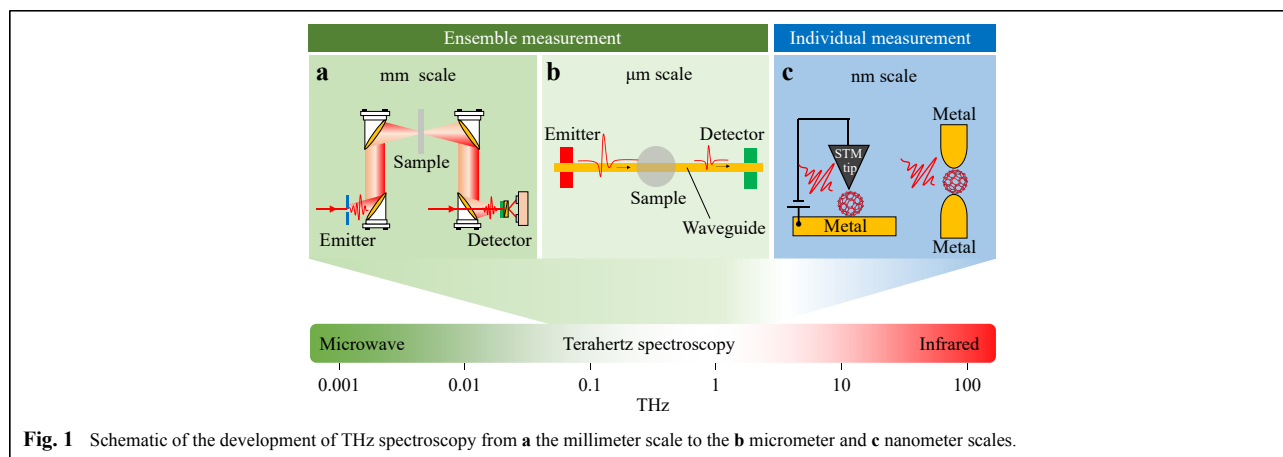


Fig. 1 Schematic of the development of THz spectroscopy from **a** the millimeter scale to the **b** micrometer and **c** nanometer scales.

describes the principles of the three types of nm-scale THz spectroscopy, that is, THz s-SNOM, THz-STM, and THz-SETS, and compares their characteristics. In Section 3, we provide a detailed description of THz-SETS and discuss the crucial aspects for achieving ultrahigh-sensitivity measurements. Section 4 presents examples of nm-scale THz dynamics revealed by THz-SETS to demonstrate the effectiveness of this technique. Finally, in Section 5, we conclude this review and provide an outlook on how nm-scale THz spectroscopy will advance the cutting edge of THz technologies and related nanotechnologies.

Principles of nm-scale THz spectroscopy

To realize nm-scale THz spectroscopy, THz electromagnetic waves must be tightly focused onto nm-scale systems, and extremely weak absorption must be detected with high sensitivity. Depending on the method used to detect the extremely weak THz absorption, nm-scale THz spectroscopy techniques can be classified into the following three categories: (i) THz s-SNOM, (ii) THz-STM, and (iii) THz-SETS. Table 1 shows a comparison of the three methods, and their characteristics are described below.

THz s-SNOM

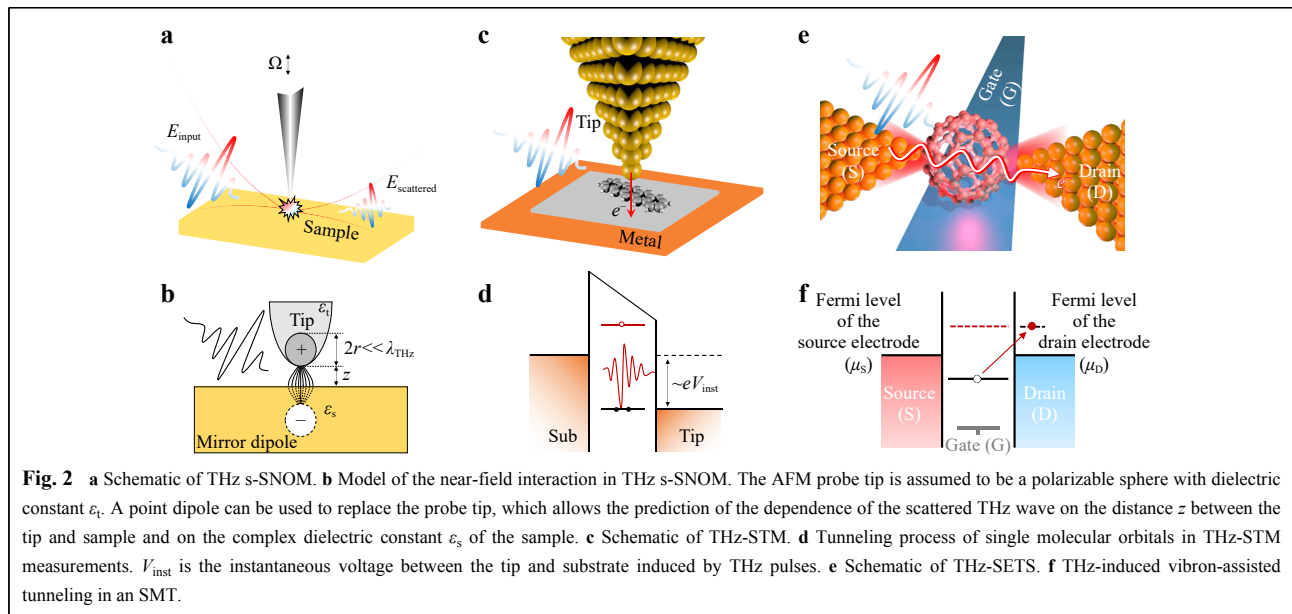
THz s-SNOM^{33–38} provided a breakthrough in the diffraction limit in free-space optics and enabled the measurement of nm-scale samples, as shown in Fig. 2a. A metal-coated atomic force microscopy (AFM) tip is used as an antenna to concentrate incident THz radiation to a nm-scale near-field spot at the tip apex. When the tip is close to the sample surface, the near-field interaction between the tip and sample modifies the tip-scattered THz field, which depends on the local dielectric properties of the sample. By collecting the scattered THz light in the far field, THz spectroscopy and imaging can be achieved at the nm scale.

The near-field interaction between the tip and sample is the key to the THz s-SNOM technique. The THz s-SNOM system can be regarded as a simple model that includes the tip and the sample, as shown in Fig. 2b. The effective polarizability of the coupled tip-sample system (α_{eff}) can be expressed by the polarizability of the tip (α) and the dielectric surface response function of the sample (β)⁵⁵.

$$\alpha_{\text{eff}} = \frac{\alpha(1+\beta)}{1-\alpha\beta/(16\pi(r+z)^3)} \quad (1)$$

Table 1 Comparison of THz s-SNOM, THz-STM, and THz-SETS.

	THz s-SNOM	THz-STM	THz-SETS
Imaging	yes	yes	no
Gating at the nm scale	difficult	difficult	easy
Requires powerful THz source	yes	yes	no
Signals	scattered power	photocurrent	photocurrent



$$\alpha = 4\pi r^3 \frac{\varepsilon_t - 1}{\varepsilon_t + 2} \quad (2)$$

$$\beta = \frac{\varepsilon_s - 1}{\varepsilon_s + 1} \quad (3)$$

where r is the radius of the assumed polarizable sphere at the tip, z represents the distance between the tip and sample, and ε_t and ε_s are the dielectric constants of the tip and sample, respectively. Typically, the tip is used in tapping mode, and by detecting the scattered THz signal at the tapping frequency, the weak signal from nm-scale regions can be extracted from the overwhelming background radiation. The THz signal from the sample can be obtained by measuring only the scattered component of the THz field (E_s) because E_s is proportional to $\alpha_{\text{eff}}E_i$ (E_i is the incident THz field). Using this technique, THz intersublevel transitions in single QDs have been measured^{33,36,37}. However, owing to the very weak backscattered light, a powerful THz radiation source, such as a free electron laser, is required.

THz-STM

THz-STM^{39–48} is another method that uses a nanoprobe. The essential difference from THz s-SNOM is that the signal measured in this method is the tunneling current instead of the scattered light power. Owing to the ultrahigh spatial resolution of STM imaging, nm-scale samples can be well resolved. As shown in Fig. 2c, a nm-scale sample is placed between an atomically sharp tip and a conducting substrate, and pulsed THz radiation is focused onto the sample. To avoid hybridization between the electronic orbitals of the sample and substrate, the substrate surface is sometimes covered by a very thin insulating layer⁴⁶. When a THz pulse is coupled to the STM tip, it generates an ultrafast voltage transient and forms a THz-induced tunneling photocurrent between the atomically sharp tip and sample, as shown in Fig. 2d. To overcome the large binding energies of electronic orbitals in molecules, strong incident THz fields are typically necessary. Owing to the high sensitivity and high spatial resolution of THz-induced tunneling photocurrent measurements, THz-STM can map the shapes of the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) wavefunctions⁴⁶.

Extensive THz s-SNOM and THz-STM measurements have been performed to study nanostructures and molecules. For more details, please refer to an excellent recently published review article⁵⁶.

THz-SETS

THz-SETS is a simple and powerful nm-scale THz

spectroscopy method that was recently developed^{49–54}. THz-SETS is based on a single-electron transistor (SET) geometry, as shown in Fig. 2e. The source and drain electrodes are separated by a gap on the order of sub-nanometer to a few tens of nanometers and focus THz electromagnetic waves onto a nm-scale system captured in the nanogap. Although it lacks imaging capabilities, the great advantage of the SET geometry is that, by using the gate electrode, the electrochemical potential and the charge state in the nanostructures can be precisely tuned, as shown in Fig. 2f. The ability to change the electrochemical potential is particularly important for the study of QDs and molecules, whose electron dynamics are strongly modulated by the electron number. When a QD or single molecule is illuminated by THz radiation, a very small but finite THz-induced photocurrent is generated. Furthermore, excitation spectra associated with intersublevel transitions or molecular vibrations can be obtained.

THz-SETS has an invaluable advantage over the other two methods, as summarized in Table 1. The THz-SETS geometry allows the modulation of the electrostatic potential and the number of conducting electrons in nanostructures by using a gate electrode. Because of this ability to tune the band structure of nanostructures, even very weak THz radiation from a blackbody light source can photoexcite electrons and produce photocurrent signals. Otherwise, intense THz light pulses are required to photoionize nanostructures.

THz-SETS using metal nanogap electrodes and single-electron tunneling measurements

In this section, we explain additional details of THz-SETS and demonstrate how it works by introducing examples involving single InAs self-assembled QDs and single molecules.

Focusing THz electromagnetic waves on nm-scale systems

To collect the maximum amount of THz power on a nm-scale sample, a solid immersion lens and metal nanogap electrodes integrated with a THz antenna structure are used, as schematically shown in Fig. 3a. A high-resistivity Si is used to make the hyperhemispherical lens. A THz electromagnetic wave is further focused into the nanogap region owing to the antenna effect of the source–drain electrodes, which greatly enhances the THz field in the nanogap area. Nanogap electrodes with various gap sizes (typically 20–50 nm) are fabricated using standard electron-beam (EB) lithography and subsequent Ti/Au deposition for the measurement of InAs QDs^{49,51,52}, InAs quantum dashes (QDHs)⁵⁰, InAs NWs, and CNTs¹³, as

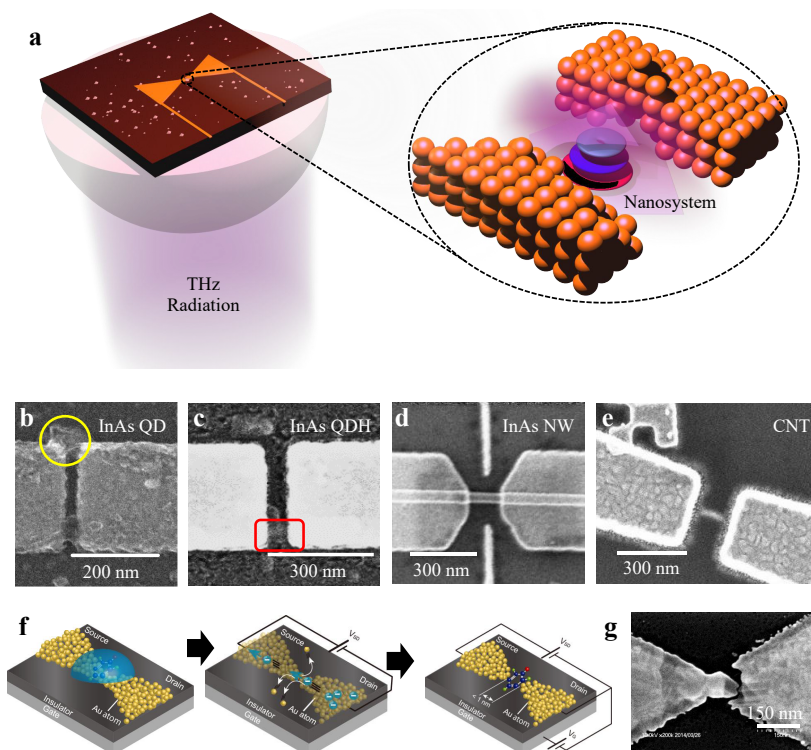


Fig. 3 **a** Schematic of the THz-SETs measurement setup⁴⁹. **b** Scanning electron microscopy (SEM) image of an InAs QD-SET⁵¹. **c** SEM image of an InAs QDH-SET⁵². **d** SEM image of an InAs NW-SET. **e** SEM image of a CNT-SET¹³. **f** Schematic of the fabrication process of 1-nm-scale metal nanogaps for capturing a single molecule, including the fabrication of metal nanojunctions, deposition of a molecular solution, and breaking of metal nanojunctions by feedback-controlled EM. **g** SEM image of the nanogap region after the EM process⁵³. Images reprinted with the following permissions: **a** and **b** from ACS, **c** from APS, and **g** from Springer Nature.

shown in Fig. 3b–e.

For measuring systems in deep-nm regions, such as single molecules, the standard top-down nanofabrication process using EB lithography does not work. Instead, a technique called the “electrical break junction” method is used to reproducibly generate sub-nm gaps. The entire process of sub-nm gap fabrication can be separated into two steps. First, a metal nanojunction is fabricated on a substrate using a technique called “shadow evaporation”⁵⁷. Then, a solution of molecules is deposited on the nanojunction, and the feedback-controlled electromigration (EM) technique^{58–60} is applied to create a nanogap to capture a single molecule, as schematically shown in Fig. 3f. The electrical break junction process with feedback control enables the reproducible fabrication of sub-nm gaps, as shown in Fig. 3g.

The THz field in the nanogap area is greatly enhanced from its value in free space because the incident THz light is squeezed into the nanogap region owing to the antenna effect. The enhancement factor of the THz field was quantitatively estimated by measuring the strength of the photon-assisted tunneling effect^{61,62}, reaching values as high as $\sim 10^5$. This enhancement factor can be well explained by

the fact that radiation with a wavelength (λ) of $\sim 100 \mu\text{m}$ is squeezed into a gap (d) of $\sim 1 \text{ nm}$, that is, the enhancement factor is $\sim \lambda/d$.

Detecting absorption by single nm-scale systems through photocurrent measurements

The enhanced THz electromagnetic field on single QDs or molecules induces photoexcitation. However, reading such signals is not trivial. In QDs and molecules, electronic states are quantized, and only a few conduction electrons can be excited by the THz field. Therefore, the detection of such few-electron absorption by conventional transmission or reflection measurements is extremely difficult. To overcome this problem, nanogap electrodes are used as source/drain electrodes to form a transistor structure for nm-scale systems (QDs, molecules, etc.), and the photocurrent is measured through the transistor. The photocurrent is induced by THz photoexcitation in the QDs or molecules, either by intersublevel transitions or by THz-excited molecular vibrations. This makes the measurement sensitive only to the THz power absorbed by the sensing target. Furthermore, to suppress thermal fluctuations and thermal broadening effects in THz photocurrent

measurements, the sample is typically cooled to the temperature of liquid helium (~ 4.2 K), at which the sample functions as an SET. In the Coulomb blockade region of SETs, the dark current is suppressed, and hence, the noise in the photocurrent measurements is very small; a photocurrent as small as ~ 10 fA can be detected.

To obtain the photocurrent spectra, Fourier transform spectroscopy or THz autocorrelation measurements with femtosecond laser pulses are used, as shown in Fig. 4a, b. The differences between the two systems are as follows. The former employs a blackbody radiation source that provides weak, broadband, and continuous THz electromagnetic waves. The latter delivers THz pulses whose intensity has a peak mainly at low frequencies (~ 1 THz for THz photoconductive antennas and several THz for semiconductor surface emitters), as shown in Fig. 4c. Although the THz light sources are different, both methods measure THz autocorrelation signals using a Michelson interferometer. The photocurrent through the SET structure is measured as a function of the position of the moving mirror. Then, THz spectra are obtained by calculating the Fourier spectra of the measured autocorrelation waveforms of the photocurrent, which contain information on THz excitation in nm-scale systems.

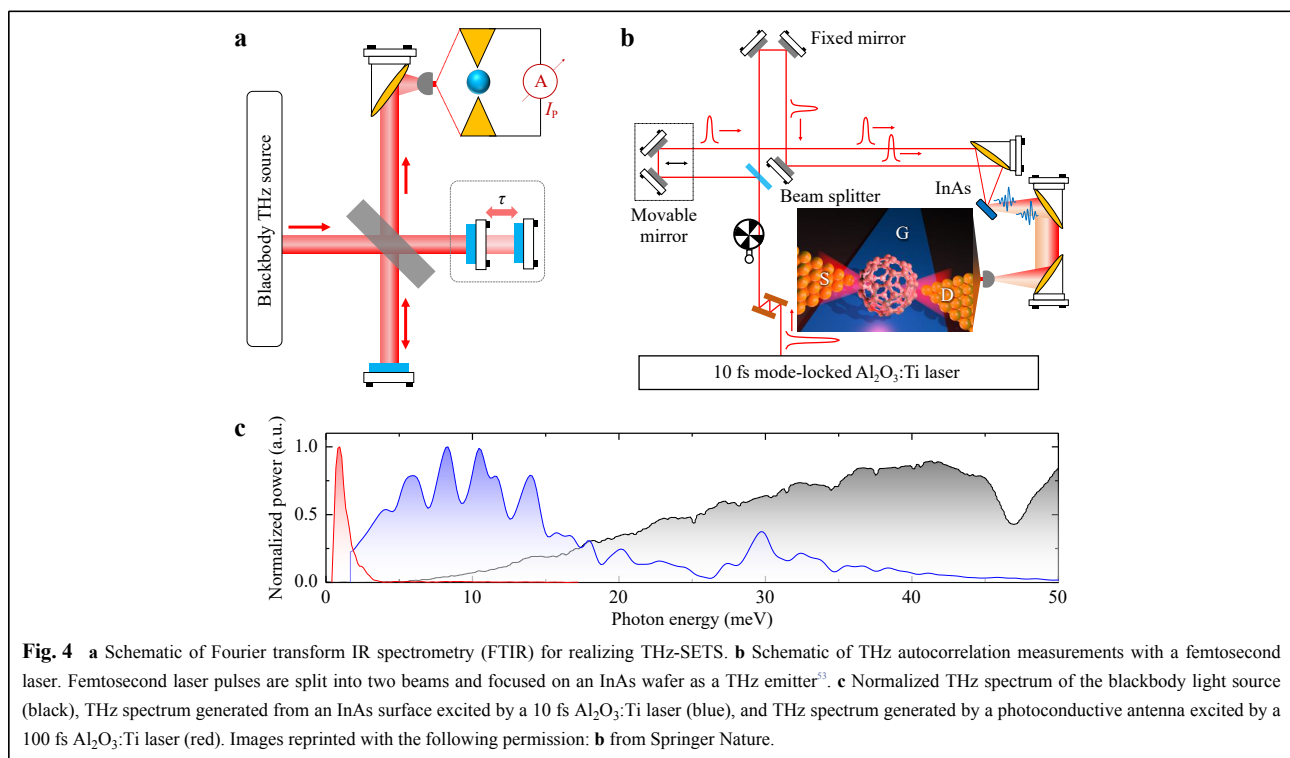
Quantum dynamics detected by THz-SETS

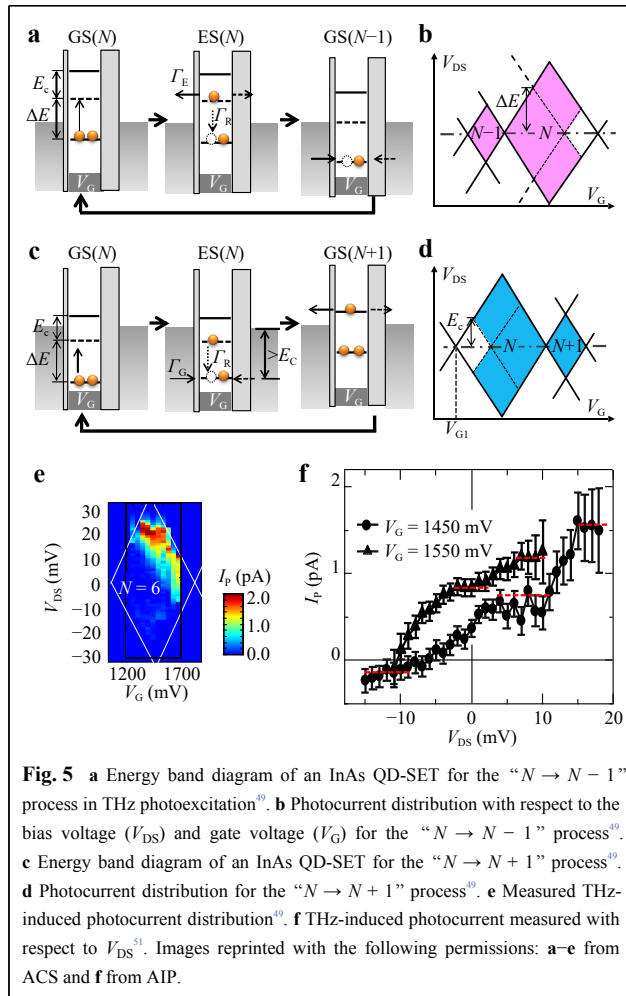
In this section, we present examples of THz signals in two types of nanostructures: self-assembled InAs QDs and fullerene molecules. These examples demonstrate the effectiveness of THz-SETS as a powerful tool for exploring nm-scale THz physics.

THz intersublevel transitions in single QDs

Self-assembled InAs QDs are a promising material system for realizing quantum effect devices, such as QD lasers and single-photon sources⁶³. The key feature of self-assembled QDs is their zero-dimensional discrete energy levels. The realization of quantum effect devices requires precise information on the energy-level structures in QDs. THz intersublevel transitions in single InAs QDs were studied using THz-SETS. Taking advantage of THz spectra with narrow linewidths and high signal-to-noise ratios, the transition dynamics and electron-electron interactions can be studied at the single- or few-electron level.

Fig. 5a, c show schematic energy band diagrams of a QD-SET, which illustrate the mechanisms of photocurrent generation by THz photoexcitation. In a self-assembled InAs QD, the energy states are quantized owing to three-dimensional confinement. A backgate is used to modulate the electrostatic potential in the QD. When the QD is illuminated by a broadband blackbody light source, an electron from a lower-energy state transitions to a higher-





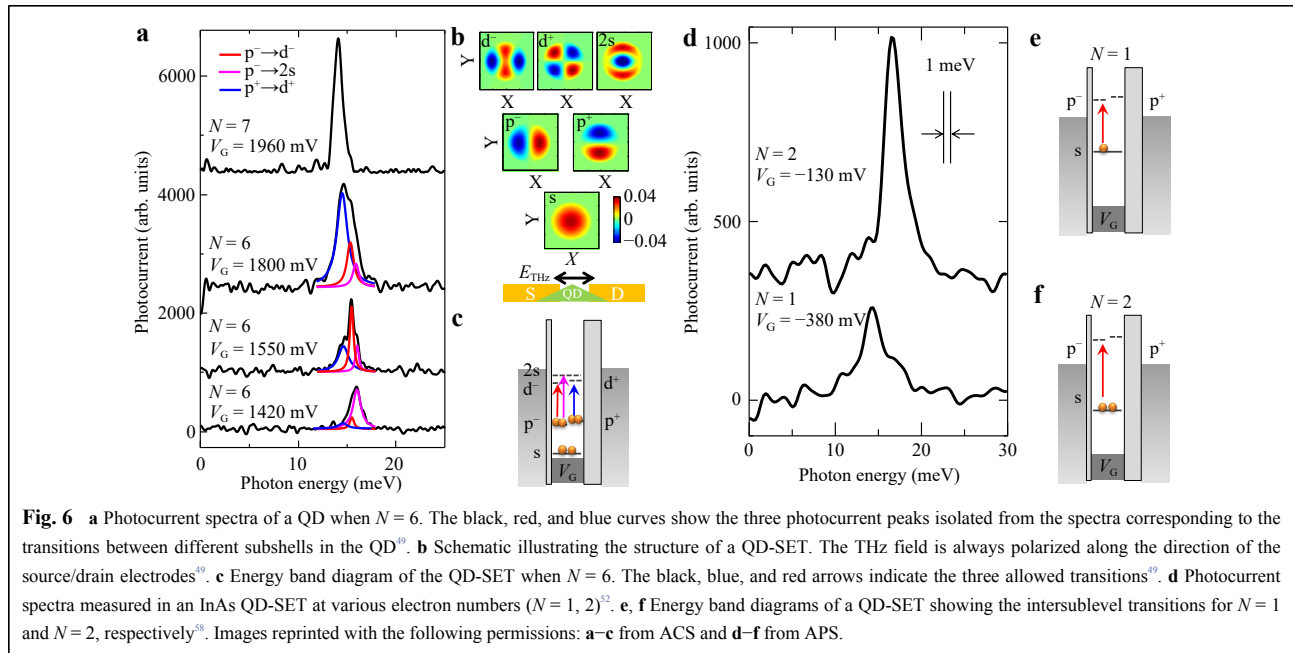
energy state by absorbing a THz photon. Then, the excited electron tunnels into one of the source/drain electrodes, and an electron from one of the electrodes tunnels into the empty lower state. Depending on the position of the electrochemical potential in the QD, the electron tunneling-in and tunneling-out processes can have different sequences, which are called the “ $N \rightarrow N - 1$ ” and the “ $N \rightarrow N + 1$ ” processes⁴⁹, as shown in Fig. 5a, c, respectively. Fig. 5b, d show schematics of the photocurrent distributions of the “ $N \rightarrow N - 1$ ” and “ $N \rightarrow N + 1$ ” processes, respectively. Fig. 5e plots the measured photocurrent with respect to the source–drain voltage (V_{DS}) and gate voltage (V_G). Comparing the experimental results and theoretical predictions, the photocurrent distribution shown in Fig. 5e indicates that the induced photocurrent arises from the “ $N \rightarrow N + 1$ ” process. Fig. 5f shows the measured photocurrent as a function of the bias voltage (V_{DS}). The photocurrent through the QD-SET is on the order of 1 pA and exhibits a stepwise increase with increasing V_{DS} , which is caused by the discrete nature of

the energy states and the Coulomb repulsion in the QD. It should be noted that there is a finite photocurrent even at $V_{DS} = 0$, indicating that the photocurrent mechanism consists of not only a simple photoconduction effect but also a photovoltaic effect. This photovoltaic effect originates from the inherent asymmetry in the four tunneling rates between the QD and the source/drain electrodes for the ground and excited states^{13,51} and may be useful in nanoscale energy harvesting in the THz range⁵¹.

Photocurrent spectra can be obtained using a Fourier transform spectrometer⁴⁹, as shown in Fig. 6a. When the electron number in the QD (N) is six, the s- and p-shells in the QD are fully occupied. Three photocurrent peaks are present at slightly different photon energies. When V_G is swept to modulate the electrostatic potential in the QD, the relative heights of the three peaks vary, but their photon energies remain constant. The three photocurrent peaks can be explained by the three transitions allowed by the optical selection rule for intersublevel photoexcitation. As shown in Fig. 6b, the THz field of this experimental setup is polarized along the source/drain nanogap electrodes, and only three dipole transitions are allowed when $N = 6$, as shown in Fig. 6c. Fig. 6c demonstrates that THz-SETS is a powerful tool for resolving very small energy splitting caused by the asymmetry in the shape of the QD.

Another advantage of THz-SETS is that the electron number in the QD can be precisely controlled by V_G . This is crucial for studying QDs or other zero-dimensional nanomaterials because both the optical and electrical properties are strongly affected by electron–electron interactions. A simple example of electron–electron interactions in QDs is shown in Fig. 6d–f. Fig. 6d plots the photocurrent spectra measured in a QD-SET when setting $N = 1$ and $N = 2$ by modulating V_G ⁵⁰. As shown, photocurrent peaks are observed at different photon energies, ~ 14.3 meV for $N = 1$ and ~ 16.7 meV for $N = 2$. As schematically shown in Fig. 6e, f, the QD can accommodate two electrons in the ground state (s-state). The optical selection rule allows only one transition from the s-state to the p-state because the THz field is polarized along the source/drain nanogap electrodes. Therefore, the two photocurrent spectra shown in Fig. 6d arise from the same transition but with different electron numbers. The different photon energies imply that adding or removing a single electron to/from the QD substantially changes the THz photoexcitation energy through electron–electron interactions. This effect is important for the design of THz sensors or emitters using intersublevel transitions in zero-dimensional nanomaterials.

THz dynamics in single fullerene molecules



Spectroscopy at the single-molecule level provides key knowledge for customized medical, genomic, chemical, and quantum information technologies. However, there is a very large mismatch between the wavelength of a THz electromagnetic wave ($\sim 100 \mu\text{m}$) and the size of a single molecule ($\sim 1 \text{ nm}$), which makes efficient focusing of THz electromagnetic waves onto a single molecule extremely difficult owing to the diffraction limit. THz spectroscopy of single fullerene and single endohedral metallofullerene molecules was performed. Ultrafast motions were observed not only for the fullerene cage⁵³ but also for the encapsulated metal atom⁵⁴.

First, we discuss how THz excitation modifies electron transport through a single molecule⁵¹. Assume there are N electrons in the molecule and that the system is in the Coulomb blockade region, as shown in Fig. 7a. The LUMO is above the source/drain Fermi levels. Therefore, in the dark, a tunneling electron cannot enter the molecular state. However, when the molecule is illuminated by THz radiation, an electron can move into the LUMO by absorbing a quantum of molecular vibration (“vibron”). The electron excited to the LUMO level subsequently leaves the molecule and tunnels into one of the electrodes, as shown in Fig. 7b (vibron-assisted tunneling-in process). Similarly, when there are $N + 1$ electrons in the molecule, and V_{DS} and V_{G} are set in the Coulomb blockade region, the HOMO is below the Fermi levels (see Fig. 7c), and the electron in the HOMO cannot escape the molecule in the dark. However, when the molecule is illuminated by THz radiation, the electron in the molecule absorbs a vibron and

can leave the molecule (vibron-assisted tunneling-out process). Subsequently, as shown in Fig. 7d, the empty HOMO is refilled by a new tunneling electron from one of the electrodes. Fig. 7e, f show maps for the dark current and the THz-induced photocurrent measured as a function of V_{G} and V_{DS} on a single-molecule transistor (SMT)⁵⁴. In Fig. 7e, the boundaries of the Coulomb diamonds are clearly shown, and it is evident that the polarity of the dark current follows the polarity of V_{DS} . In contrast, as shown in Fig. 7f, the THz-induced photocurrent does not depend on the bias voltage for the range plotted in the figure, indicating that a portion of the photocurrent arises from the photovoltaic mechanism, similar to the photocurrent observed in QD-SETs⁵¹.

Fig. 8a shows an autocorrelation trace of the THz-induced photocurrent signal measured on a C_{60} SMT. The trace shows quasi-oscillatory behavior with periods of ~ 1 and $\sim 2 \text{ ps}$. The corresponding Fourier spectrum in Fig. 8b exhibits two low-energy peaks at ~ 2 and $\sim 4 \text{ meV}$, which arise from the THz center-of-mass nanomechanical oscillation of the fullerene cage⁵³. When a C_{60} molecule is captured on the surface of the Au nanogap electrodes, the C_{60} molecule experiences a quasi-parabolic van der Waals potential, which gives rise to a quasi-harmonic oscillation of the entire C_{60} molecule against the Au wall (center-of-mass oscillation). When the electron number in the molecule changes, the profile of the van der Waals potential may be modified. As shown in Fig. 8b, the photocurrent peaks at ~ 2 and $\sim 4 \text{ meV}$ are both finely split into two peaks. The observed peak splitting agrees well

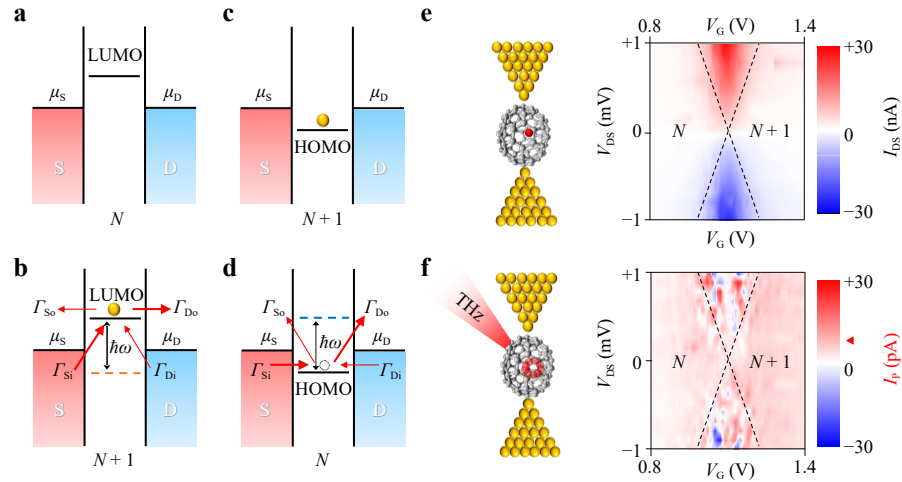


Fig. 7 **a, b** THz-induced vibron-assisted tunneling process when V_G is on the left side of the charge degeneracy point. **c, d** THz-induced vibron-assisted tunneling process when V_G is on the right side of the charge degeneracy point. Γ_{Si} : tunnel-in rate from the source; Γ_{Di} : tunnel-in rate from the drain; Γ_{So} : tunnel-out rate to the source; Γ_{Do} : tunnel-out rate to the drain⁵⁴. Maps of the **e** dark current (I_{DS}) and **f** THz-induced photocurrent (I_P) of an SMT as a function of V_{DS} and V_G . Images reprinted with the following permissions: **a–f** from IOP.

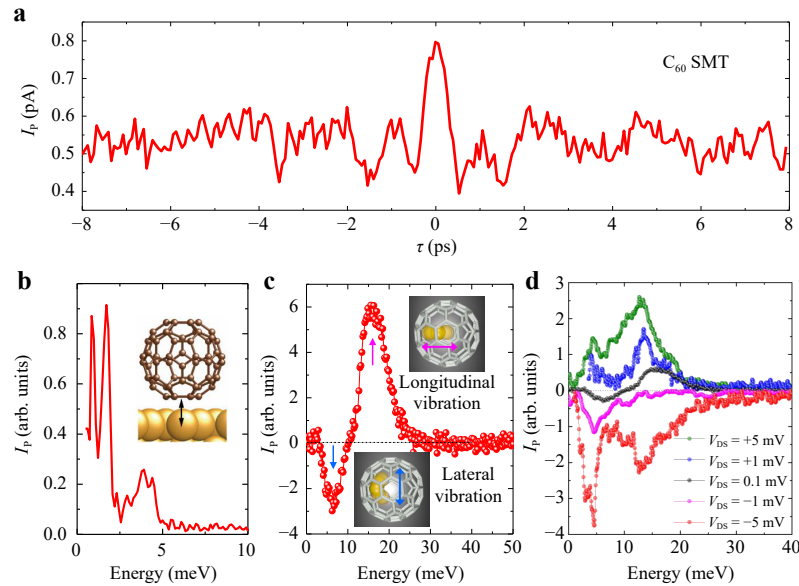


Fig. 8 **a** Quasi-autocorrelation trace (interferogram) of the THz-induced photocurrent measured on a C_{60} SMT. τ is the time difference between the two consecutive applied THz pulses. **b** Fourier spectrum of the interferogram shown in **a**. The spectrum exhibits sharp peaks at ~ 2 and ~ 4 meV with very fine peak splitting⁵³. **c** THz-induced photocurrent spectrum of an SMT that consists of a single $Ce@C_{82}$ molecule⁵⁴. **d** Magnitudes of the two photocurrent peaks as a function of V_{DS} ($-5 \text{ mV} < V_{DS} < 5 \text{ mV}$)⁶⁵. Images reprinted with the following permissions: **a** and **b** from Springer Nature and **c** and **d** from IOP.

with the calculated change in the curvature of the quasi-harmonic van der Waals potential. This observation demonstrates that even the difference in the vibrational frequency caused by single-electron charging in the molecule can be detected by THz-SETS using nanogap electrodes⁵³.

Furthermore, THz-SETS can reveal the dynamics of a single atom. A single $Ce@C_{82}$ fullerene molecule was

captured by a sub-nm gap between metal electrodes and excited by a THz electromagnetic wave to probe the motion of the Ce atom⁵⁴. Two photocurrent peaks in the THz frequency range were observed, as shown in Fig. 8c, d. The first peak at ~ 5 meV is assigned to the vibration of the trapped Ce atom in the lateral direction, and the second broader peak at ~ 15 meV is attributed to the vibration of the Ce atom in the longitudinal direction^{54,64,65}. As seen in

Fig. 8c, d, the two peaks are broader than the photocurrent peaks in Fig. 8b. The broad peaks suggest that the vibrational modes of the Ce atom have very short coherence times, which is probably due to the chaotic interactions between the elastic fullerene cage and the Ce atom. These results demonstrate that THz-SETS has an extremely high sensitivity and can sense the dynamic motion of a single atom.

These examples clearly demonstrate that although THz-SETS is not capable of imaging, it can provide invaluable information on the electronic and vibronic dynamics in deep-nm-systems with a sub-picosecond time resolution.

Conclusion and outlook

In summary, we have reviewed a novel THz spectroscopy technique for deep-nm-scale systems by combining antenna-integrated metal nanogap electrodes with an SET structure. Metal nanogap electrodes can capture a single nm-scale system, such as a semiconductor QD or a single molecule. The THz field is tightly confined in the metal nanogap region and is enhanced by a factor of $\sim \lambda/d$ (λ : THz wavelength, d : gap size), which can reach $\sim 10^5$. Even tiny absorption of THz radiation by a single nm-scale system can be detected by measuring the THz-induced photocurrent through the system. Taking advantage of the ultrasmall dark current in the Coulomb blockade regions in single-electron tunneling, THz dynamics, such as intersublevel transitions in single QDs and vibrational excitations in single molecules, can be studied. The THz-SETS scheme can achieve THz spectroscopy with simultaneous sub-nm-scale spatial resolution and sub-picosecond time resolution.

The ability to measure the properties of single molecules may be useful for studying complex molecules, such as DNA and biological macromolecules, at the single-molecule level. In conventional THz spectroscopy, THz plasmonic nanoantennas^{66,67} and THz metamaterials^{68–71} have been used to enhance THz fields for the detection of microorganisms, organic molecules, and biomolecules. However, ensemble measurements contain information on both intra- and intermolecular vibrations. Because of the complex nature of biomolecules, these two types of vibrations are easily coupled and exhibit very broad absorption peaks, which makes THz data interpretation difficult. Measuring such complex molecules at the single-molecule level is promising because it can remove the effects of both intermolecular excitations and inhomogeneous broadening.

There are several issues that must be solved for nm-scale THz spectroscopy. One issue is how to image and capture targeted ultrasmall nanostructures (such as single

molecules) while maintaining the ability to modulate the electrostatic potential and the electron number in the nanostructures. As mentioned previously, s-SNOM and STM are excellent at imaging nanostructures⁴⁶. However, a major drawback is that it is difficult to modulate the electronic states of the sample using these nanoprobe techniques because they lack gate electrodes. A few novel methods based on nanoprobe techniques have been developed^{72–75} that include both “imaging” and “gating” functions simultaneously. However, realizing this dual functionality at the single-molecule level remains a major challenge. The SET geometry can easily modulate the electronic states in single molecules. However, capturing single molecules using nanogap electrodes is a stochastic process, and contact cannot be made at a targeted molecule. Therefore, combining the two types of measurements to realize a more versatile nanoscale THz spectroscopy system in the near future is highly desirable.

We conceive a new direction for THz-SETS: the control of the electronic/vibronic states in nm-scale systems, which will be critical for future quantum information technologies. When THz photons strongly couple with electrons in nanostructures^{76,77}, they can form a quantum hybrid system: THz cavity quantum electrodynamics (cavity-QED)^{78–80}. The strong electron–photon coupling in THz cavity-QED enables the operation of the cavity quantum dynamic ground state⁷⁸ and is expected to be useful for transferring quantum information from electrons to photons and vice versa⁸¹. This is a new technology for quantum information processing. THz-SETS is attractive for THz cavity-QED because it can tightly focus THz radiation onto a single quantum nanostructure. Furthermore, its gating ability enables the manipulation of quantum states using simple electrical gating. However, the quality (Q)-factors of standard bowtie-type THz antennas used for THz-SETS are too small to achieve strong electron–photon coupling (typically Q-factor of ~ 1). By combining the present THz-SETS with high Q-factor THz cavities, such as THz metamaterials^{78,79} and THz photonic crystals⁸⁰, a powerful platform can be developed for studying THz cavity-QED.

Nanoscale THz spectroscopy also shows promise for the investigation of THz nonlinear effects, in which an intense THz field is utilized to reveal new light–matter interactions^{82,83}. Many exciting findings have been reported, such as the use of intense THz pulses to coherently control the switching of the polarization in ferroelectric materials^{84,85} and to excite/control spin waves in antiferromagnetic materials^{86–91}. Such findings indicate that intense THz waves can control material properties and even lattice structures. The nanoscale THz spectroscopy

introduced here can extend such nonlinear control to nm-scale regions. In particular, when the THz field is strongly squeezed into sub-nm regions, it is greatly enhanced by a factor of $\sim 10^5$. The combination of a recently developed technique to generate very intense THz pulses^{83,92,93} with such a large field enhancement effect in nanogaps offers a unique opportunity to study novel material properties in the extremely high THz electric field regime (1–100 GV/cm).

In conclusion, THz-SETS provides a powerful method for squeezing THz electromagnetic waves into nm-scale regions and detecting ultrasmall THz absorption with high sensitivity. It is promising for the investigation of the nm- and sub-nm-scale THz dynamics of not only single quantum nanostructures but also single molecules, which will extend the great success of traditional THz spectroscopy to the deep-nm-scale regime. Such nm-scale THz spectroscopy provides a key scientific foundation for nanoscience and nanotechnology.

Acknowledgements

The authors thank Y. Arakawa, G. Bastard, H. Q. Xu, Y. Hirayama, K. Yoshida, K. Shibata, and T. Tsurugaya for their fruitful discussions. This work was supported by MEXT KAKENHI Grant Number JP15H05868, JSPS KAKENHI Grant Numbers JP20H05660, JP17H01038, JP16H06709, and the Canon Science Foundation.

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Conflict of interest

The authors declare no conflicts of interest.

Received: 10 January 2021 Revised: 15 November 2021 Accepted: 28 November 2021

Published online: 13 December 2021

References

1. Tonouchi, M. Cutting-edge terahertz technology. *Nature Photonics* **1**, 97–105 (2007).
2. Kawase, K. et al. Non-destructive terahertz imaging of illicit drugs using spectral fingerprints. *Optics Express* **11**, 2549–2554 (2003).
3. Mittleman, D. M. et al. Recent advances in terahertz imaging. *Applied Physics B* **68**, 1085–1094 (1999).
4. Mittleman, D. M. Twenty years of terahertz imaging [Invited]. *Optics Express* **26**, 9417–9431 (2018).
5. Jansen, C. et al. Terahertz imaging: applications and perspectives. *Applied Optics* **49**, E48–E57 (2010).
6. Beard, M. C., Turner, G. M. & Schmuttenmaer, C. A. Terahertz spectroscopy. *J. Phys. Chem. B* **106**, 7146–7159 (2002).
7. Jepsen, P. U., Cooke, D. G. & Koch, M. Terahertz spectroscopy and imaging—Modern techniques and applications. *Laser & Photonics Reviews* **5**, 124–166 (2011).
8. Baxter, J. B. & Guglietta, G. W. Terahertz spectroscopy. *Analytical Chemistry* **83**, 4342–4368 (2011).
9. Taday, P. F. Applications of terahertz spectroscopy to pharmaceutical sciences. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **362**, 351–364 (2004).
10. Drexler, H. et al. Spectroscopy of quantum levels in charge-tunable InGaAs quantum dots. *Physical Review Letters* **73**, 2252–2255 (1994).
11. Hameau, S. et al. Strong electron-phonon coupling regime in quantum dots: evidence for everlasting resonant polarons. *Physical Review Letters* **83**, 4152–4155 (1999).
12. He, X. W. et al. Carbon nanotube terahertz detector. *Nano Letters* **14**, 3953–3958 (2014).
13. Tsurugaya, T. et al. Terahertz spectroscopy of individual carbon nanotube quantum dots. *Nano Letters* **19**, 242–246 (2019).
14. Joyce, H. J. et al. Electronic properties of GaAs, InAs and InP nanowires studied by terahertz spectroscopy. *Nanotechnology* **24**, 214006 (2013).
15. Peng, K. et al. Single nanowire photoconductive terahertz detectors. *Nano Letters* **15**, 206–210 (2015).
16. Han, P. Y. & Zhang, X. C. Free-space coherent broadband terahertz time-domain spectroscopy. *Measurement Science and Technology* **12**, 1747–1756 (2001).
17. Beard, M. C., Turner, G. M. & Schmuttenmaer, C. A. Transient photoconductivity in GaAs as measured by time-resolved terahertz spectroscopy. *Physical Review B* **62**, 15764–15777 (2000).
18. Beard, M. C., Turner, G. M. & Schmuttenmaer, C. A. Subpicosecond carrier dynamics in low-temperature grown GaAs as measured by time-resolved terahertz spectroscopy. *Journal of Applied Physics* **90**, 5915–5923 (2001).
19. Stringer, M. R. et al. The analysis of human cortical bone by terahertz time-domain spectroscopy. *Physics in Medicine & Biology* **50**, 3211–3219 (2005).
20. Heiliger, H. M. et al. Low-dispersion thin-film microstrip lines with cyclotene (benzocyclobutene) as dielectric medium. *Applied Physics Letters* **70**, 2233–2235 (1997).
21. Wang, K. L. & Mittleman, D. M. Metal wires for terahertz wave guiding. *Nature* **432**, 376–379 (2004).
22. Desplanque, L., Lampin, J. F. & Mollot, F. Generation and detection of terahertz pulses using post-process bonding of low-temperature-grown GaAs and AlGaAs. *Applied Physics Letters* **84**, 2049–2051 (2004).
23. Wood, C. et al. On-chip pulsed terahertz systems and their applications. *International Journal of Infrared and Millimeter Waves* **27**, 557–569 (2006).
24. Cunningham, J. et al. Terahertz evanescent field microscopy of dielectric materials using on-chip waveguides. *Applied Physics Letters* **92**, 032903 (2008).
25. Kasai, S. et al. Micro strip line-based on-chip terahertz integrated devices for high sensitivity biosensors. *Applied Physics Express* **2**, 062401 (2009).
26. George, P. A. et al. Microfluidic devices for terahertz spectroscopy of biomolecules. *Optics Express* **16**, 1577–1582 (2008).
27. Tang, Q. et al. Microfluidic devices for terahertz spectroscopy of live cells toward lab-on-a-chip applications. *Sensors* **16**, 476 (2016).
28. Ju, X. J. et al. Direct writing of microfluidic three-dimensional photonic crystal structures for terahertz technology applications. *ACS Applied Materials & Interfaces* **11**, 41611–41616 (2019).
29. Nagel, M. et al. Integrated THz technology for label-free genetic diagnostics. *Applied Physics Letters* **80**, 154–156 (2002).
30. Nagel, M. et al. Integrated planar terahertz resonators for femtomolar sensitivity label-free detection of DNA hybridization. *Applied Optics* **41**, 2074–2078 (2002).

31. Serita, K. et al. Invited article: terahertz microfluidic chips sensitivity-enhanced with a few arrays of meta-atoms. *APL Photonics* **3**, 051603 (2018).
32. Hu, X. et al. Metamaterial absorber integrated microfluidic terahertz sensors. *Laser & Photonics Reviews* **10**, 962-969 (2016).
33. Knoll, B. & Keilmann, F. Near-field probing of vibrational absorption for chemical microscopy. *Nature* **399**, 134-137 (1999).
34. Chen, H. T., Kersting, R. & Cho, G. C. Terahertz imaging with nanometer resolution. *Applied Physics Letters* **83**, 3009-3011 (2003).
35. Wang, K. L. et al. Antenna effects in terahertz apertureless near-field optical microscopy. *Applied Physics Letters* **85**, 2715-2717 (2004).
36. Houel, J. et al. Ultraweak-absorption microscopy of a single semiconductor quantum dot in the midinfrared range. *Physical Review Letters* **99**, 217404 (2007).
37. Jacob, R. et al. Intersublevel spectroscopy on single inas-quantum dots by terahertz near-field microscopy. *Nano Letters* **12**, 4336-4340 (2012).
38. Maissen, C. et al. Probes for ultrasensitive THz nanoscopy. *ACS Photonics* **6**, 1279-1288 (2019).
39. Wu, S. W. & Ho, W. Two-photon-induced hot-electron transfer to a single molecule in a scanning tunneling microscope. *Physical Review B* **82**, 085444 (2010).
40. Terada, Y. et al. Real-space imaging of transient carrier dynamics by nanoscale pump-probe microscopy. *Nature Photonics* **4**, 869-874 (2010).
41. Dolocan, A. et al. Two-color ultrafast photoexcited scanning tunneling microscopy. *The Journal of Physical Chemistry C* **115**, 10033-10043 (2011).
42. Yoshida, S. et al. Nanoscale probing of transient carrier dynamics modulated in a GaAs-PIN junction by laser-combined scanning tunneling microscopy. *Nanoscale* **4**, 757-761 (2012).
43. Cocker, T. L. et al. An ultrafast terahertz scanning tunnelling microscope. *Nature Photonics* **7**, 620-625 (2013).
44. Eisele, M. et al. Ultrafast multi-terahertz nano-spectroscopy with sub-cycle temporal resolution. *Nature Photonics* **8**, 841-845 (2014).
45. Shigekawa, H., Yoshida, S. & Takeuchi, O. Spectroscopy: nanoscale terahertz spectroscopy. *Nature Photonics* **8**, 815-817 (2014).
46. Cocker, T. L. et al. Tracking the ultrafast motion of a single molecule by femtosecond orbital imaging. *Nature* **539**, 263-267 (2016).
47. Yoshioka, K. et al. Real-space coherent manipulation of electrons in a single tunnel junction by single-cycle terahertz electric fields. *Nature Photonics* **10**, 762-765 (2016).
48. Jelic, V. et al. Ultrafast terahertz control of extreme tunnel currents through single atoms on a silicon surface. *Nature Physics* **13**, 591-598 (2017).
49. Zhang, Y. et al. Terahertz intersublevel transitions in single self-assembled InAs quantum dots with variable electron numbers. *Nano Letters* **15**, 1166-1170 (2015).
50. Zhang, Y. et al. Probing many-body quantum states in single InAs quantum dots: terahertz and tunneling spectroscopy. *Physical Review B* **91**, 241301 (2015).
51. Zhang, Y. et al. Gate-controlled terahertz single electron photovoltaic effect in self-assembled InAs quantum dots. *Applied Physics Letters* **107**, 103103 (2015).
52. Zhang, Y. et al. Excited-state charging energies in quantum dots investigated by terahertz photocurrent spectroscopy. *Physical Review B* **93**, 235313 (2016).
53. Du, S. Q. et al. Terahertz dynamics of electron-vibron coupling in single molecules with tunable electrostatic potential. *Nature Photonics* **12**, 608-612 (2018).
54. Du, S. Q. et al. Ultrafast rattling motion of a single atom in a fullerene cage sensed by terahertz spectroscopy. *Applied Physics Express* **13**, 105002 (2020).
55. Keilmann, F. & Hillenbrand, R. Near-field microscopy by elastic light scattering from a tip. *Philosophical Transactions of the Royal Society A:Mathematical, Physical and Engineering Sciences* **362**, 787-805 (2004).
56. Cocker, T. L. et al. Nanoscale terahertz scanning probe microscopy. *Nature Photonics* **15**, 558-569 (2021).
57. Dolan, G. J. Offset masks for lift-off photoprocessing. *Applied Physics Letters* **31**, 337-339 (1977).
58. Park, H. et al. Fabrication of metallic electrodes with nanometer separation by electromigration. *Applied Physics Letters* **75**, 301-303 (1999).
59. Strachan, D. R. et al. Controlled fabrication of nanogaps in ambient environment for molecular electronics. *Applied Physics Letters* **86**, 043109 (2005).
60. Umeno, A. & Hirakawa, K. Nonthermal origin of electromigration at gold nanojunctions in the ballistic regime. *Applied Physics Letters* **94**, 162103 (2009).
61. Shibata, K. et al. Photon-assisted tunneling through self-assembled InAs quantum dots in the terahertz frequency range. *Physical Review Letters* **109**, 077401 (2012).
62. Yoshida, K., Shibata, K. & Hirakawa, K. Terahertz field enhancement and photon-assisted tunneling in single-molecule transistors. *Physical Review Letters* **115**, 138302 (2015).
63. Petroff, P., Lorke, A. & Imamoglu, A. Epitaxially self-assembled quantum dots. *Physics Today* **54**, 46-52 (2001).
64. Andreoni, W. & Curioni, A. Freedom and constraints of a metal atom encapsulated in fullerene cages. *Physical Review Letters* **77**, 834-837 (1996).
65. Andreoni, W. & Curioni, A. Ab initio approach to the structure and dynamics of metallofullerenes. *Applied Physics A* **66**, 299-306 (1998).
66. Park, H. R. et al. Colossal absorption of molecules inside single terahertz nanoantennas. *Nano Letters* **13**, 1782-1786 (2013).
67. Lee, D. K. et al. Highly sensitive and selective sugar detection by terahertz nano-antennas. *Scientific Reports* **5**, 15459 (2015).
68. Xie, L. J. et al. Extraordinary sensitivity enhancement by metasurfaces in terahertz detection of antibiotics. *Scientific Reports* **5**, 8671 (2015).
69. Park, S. J. et al. Sensing viruses using terahertz nano-gap metamaterials. *Biomedical Optics Express* **8**, 3551-3558 (2017).
70. Zhao, X. et al. Label-free self-referenced sensing of living cells by terahertz metamaterial-based reflection spectroscopy. *Biomedical Optics Express* **10**, 1196-1206 (2019).
71. Gu, H. Y. et al. Molecular methylation detection based on terahertz metamaterial technology. *Analyst* **145**, 6705-6712 (2020).
72. Kanai, Y. et al. Electrically tuned spin-orbit interaction in an InAs self-assembled quantum dot. *Nature Nanotechnology* **6**, 511-516 (2011).
73. Woessner, A. et al. Near-field photocurrent nanoscopy on bare and encapsulated graphene. *Nature Communications* **7**, 10783 (2016).
74. Mastel, S. et al. Terahertz nanofocusing with cantilevered terahertz-resonant antenna tips. *Nano Letters* **17**, 6526-6533 (2017).
75. Weng, Q. C. et al. Imaging of nonlocal hot-electron energy dissipation via shot noise. *Science* **360**, 775-778 (2018).
76. Sherwin, M. S., Imamoglu, A. & Montroy, T. Quantum computation with quantum dots and terahertz cavity quantum electrodynamics. *Physical Review A* **60**, 3508-3514 (1999).
77. Cole, B. E. et al. Coherent manipulation of semiconductor quantum bits with terahertz radiation. *Nature* **410**, 60-63 (2001).
78. Scalari, G. et al. Ultrastrong coupling of the cyclotron transition of a 2D electron gas to a THz metamaterial. *Science* **335**, 1323-1326 (2012).
79. Bayer, A. et al. Terahertz light-matter interaction beyond unity coupling strength. *Nano Letters* **17**, 6340-6344 (2017).
80. Zhang, Q. et al. Collective non-perturbative coupling of 2D electrons with high-quality-factor terahertz cavity photons. *Nature Physics* **12**,

- 1005-1011 (2016).
81. Northup, T. E. & Blatt, R. Quantum information transfer using photons. *Nature Photonics* **8**, 356-363 (2014).
82. Zhang, X. C., Shkurinov, A. & Zhang, Y. Extreme terahertz science. *Nature Photonics* **11**, 16-18 (2017).
83. Salén, P. et al. Matter manipulation with extreme terahertz light: progress in the enabling THz technology. *Physics Reports* **836-837**, 1-74 (2019).
84. Qi, T. T. et al. Collective coherent control: synchronization of polarization in ferroelectric PbTiO₃ by shaped THz fields. *Physical Review Letters* **102**, 247603 (2009).
85. Li, X. et al. Terahertz field-induced ferroelectricity in quantum paraelectric SrTiO₃. *Science* **364**, 1079-1082 (2019).
86. Grishunin, K. et al. Excitation and detection of terahertz coherent spin waves in antiferromagnetic α -Fe₂O₃. *Physical Review B* **104**, 024419 (2021).
87. Mashkovich, E. A. et al. Terahertz optomagnetism: nonlinear THz excitation of GHz spin waves in antiferromagnetic FeBO₃. *Physical Review Letters* **123**, 157202 (2019).
88. Baierl, S. et al. Terahertz-driven nonlinear spin response of antiferromagnetic nickel oxide. *Physical Review Letters* **117**, 197201 (2016).
89. Baierl, S. et al. Nonlinear spin control by terahertz-driven anisotropy fields. *Nature Photonics* **10**, 715-718 (2016).
90. Kampfrath, T., Tanaka, K. & Nelson, K. A. Resonant and nonresonant control over matter and light by intense terahertz transients. *Nature Photonics* **7**, 680-690 (2013).
91. Kampfrath, T. et al. Coherent terahertz control of antiferromagnetic spin waves. *Nature Photonics* **5**, 31-34 (2011).
92. Clerici, M. et al. Wavelength scaling of terahertz generation by gas ionization. *Physical Review Letters* **110**, 253901 (2013).
93. Yeh, K. L. et al. Generation of 10 μ s ultrashort terahertz pulses by optical rectification. *Applied Physics Letters* **90**, 171121 (2007).