Single-Molecule Continuous-Wave Terahertz Rectification Spectroscopy and Microscopy

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**ABSTRACT:** We report rectification spectroscopy (RS) for single molecules performed with continuous-wave terahertz (CW THz) radiation at the tunneling junction of a scanning tunneling microscope (STM) at 8 K. CW THz-RS serves as a new technique in single-molecule vibrational and magnetic excitation spectroscopy besides inelastic electron tunneling spectroscopy (IETS). By quantitatively studying IETS and THz RS, we show that CW THz induces a sinusoidal bias modulation with amplitude linearly dependent on the THz far-field amplitude. Such THz-induced bias modulation amplitude appears to be sensitive to the THz beam alignment but insensitive to variation in the tunneling gap far smaller than the THz wavelength.

**KEYWORDS:** scanning tunneling microscope, continuous-wave terahertz wave, rectification spectroscopy, inelastic electron tunneling spectroscopy, single-molecule spectroscopy

Rectifiers such as semiconductor and vacuum tube diodes are widely used in power electronics to convert AC into DC signals. In the context of a single molecule in a tunneling junction, nonlinearity in the $I-V$ curve, associated with inelastic electron tunneling, gives rise to rectification current from an AC bias modulation. Indeed, experiments have demonstrated atomic-scale rectification by coupling 800 MHz microwave radiation into a tunneling junction. However, single-molecule RS performed with a continuous-wave (CW) THz source has not been reported. While a signal generator provides the microwave voltage bias modulation through a coaxial cable, laser radiation freely propagating in space delivers the THz electric field oscillations into the STM junction. On the other hand, although laser-induced rectification was previously observed by coupling mid-infrared radiation into a tunneling junction, such a measurement typically requires high laser intensity and small tunneling gap to achieve a good signal-to-noise ratio. Such requirements lead to an unstable tunneling gap due to laser-induced thermal expansion and molecular mobility or reaction, and make it unsuitable for single-molecule spectroscopy. Here, the CW THz-RS technique provides a nondestructive approach for light-induced single-molecule spectroscopy in addition to IETS measurement.

Coupling ultrafast THz pulses into an STM junction generates transient voltage pulses that can induce nanoscale ultrafast dynamics. However, the voltage pulses in the tunneling junction often have a high peak intensity of up to several volts and are too strong for low-energy spectroscopy of single molecules. Moreover, obtaining high energy resolution in THz time domain spectroscopy (TDS) requires an extended delay scan range, which can be very time-consuming in application. Therefore, it is desirable to incorporate THz frequency domain spectroscopy (FDS) as a new approach for single-molecule spectroscopy. With the chemical and spatial sensitivity demonstrated for microwave RS, it is promising to implement CW THz rectification for single-molecule FDS by extending the higher THz frequency range that is not covered by IETS and electron spin resonance spectroscopy.

In this study, we demonstrated CW THz-RS for five different single-molecule species and two different substrates, extending the rectifying source frequency to the THz gap. We also quantitatively investigated the near-field voltage across the tunneling junction induced by THz radiation and the influence of its far-field intensity on the line shape and signal intensity for CW THz-RS. Figure 1a shows the experimental setup for CW THz-STM. The THz radiation was generated from a photoconductive antenna (PCA) emitter and directly focused into the STM junction. The THz field intensity is controlled by the voltage supplied to the PCA emitter ($V_{PCA}$). A square wave $V_{PCA}$ chopped the THz radiation and induced a periodic change in tunneling current (Figure 1b). The THz-induced rectification current was measured by extracting the first-harmonic component from the STM tunneling current through lock-in detection. Recording the rectification current as a

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**Received:** January 20, 2023  
**Revised:** March 27, 2023  
**Published:** March 31, 2023
function of the DC tip–substrate bias with a fixed tip height generated a THz-RS spectrum. Here, by comparing the THz-RS to IETS in both spectroscopy (Figure 1c) and imaging (Figure 1d,e) for a carbon monoxide (CO) molecule, we observed chemical sensitivity and spatial resolution for these two types of measurement.

To understand how THz far-field radiation coupled to the STM junction, we measured IETS spectra over CO on an Ag(110) surface with nonchopped THz radiation (Figure 2a). THz field intensity was controlled by tuning the DC voltage supplied to the PCA emitter (V_{PCA,C}). Under the influence of
THz-induced near-field radiation in the junction, we observed increasing peak splitting in the IETS spectra with increasing THz far-field amplitude that is consistent with a bias redistribution under THz irradiation. Assuming CW THz radiation induced a sinusoidal bias modulation in the junction with the amplitude $V_{THz}$, the IETS spectral waveform is mathematically expressed as a convolution between an IETS spectrum in the absence of THz illumination and a probability weight function of the THz-induced bias modulation:

$$S_{00}(V_0, V_{THz}) = \int_{V_0}^{V_0 + V_{THz}} S_{00}(V)w(V, V_0, V_{THz}) \, dV$$

(1)

Here, $V_0$ is the DC bias across the tunneling junction, $S_{00}(V)$ is the THz-free IETS waveform, and $w(V, V_0, V_{THz})$ is the weight function representing the normalized probability distribution of the THz-induced voltage. The weight function for a sinusoidal bias modulation is written as

$$w(V, V_0, V_{THz}) = \frac{1}{\sigma \sqrt{V_{THz}^2 - (V - V_0)^2}} \text{ for } V - V_0 < V_{THz}$$

(2)

Fitting each IETS spectrum in Figure 2a according to eqs 1 and 2, we obtained $V_{THz}$ as a function of $V_{PCAL}$ (Figure 2b). The fitted $V_{THz}$ follows a trend similar to that of the THz photocurrent detected by the PCA receiver (Rx photocurrent) using ambient detection as a function of the $V_{PCAL}$ used for THz generation (see section III in the Supporting Information for details of the ambient detection method). Plotting fitted $V_{THz}$ against Rx photocurrent, we obtained a linear relation between the two variables with a slope of 0.013 mV/nA (Figure 2c). Since the Rx photocurrent is proportional to the THz far-field amplitude $E_{THz}$, we can claim that $V_{THz}$ is linearly proportional to $E_{THz}$ with the slope indicating the relative near-field enhancement in the STM junction.

Using this calibration method, we measured $V_{THz}$ induced by nonchopped 0.150 THz radiation at different tip–substrate distances (Figure 2d) and found it to be nearly constant within the measured range of tunneling gap. When the tip–substrate distance is far smaller than the THz wavelength, field retardation is negligible and the THz quasi-static near-field in the junction can lead to constant amplitude in the THz-induced voltage in the STM junction. The tip–substrate gap range used for measurement is estimated to be from 3.2 to 4.2 Å (see details for the estimation of tunneling gap in section IV in the Supporting Information). Therefore, the quasi-static approximation is valid for the full range of THz frequency (0.050–1.290 THz) provided by our experimental setup, with a wavelength of ~2 mm at 0.150 THz.

To further investigate how THz field intensity affects the rectification signal, we measured THz-RS spectra of the same CO molecule with different THz far-field amplitude $E_{THz}$ (Figure 3a). We resolved both hindered translation (HT) and hindered rotation (HR) modes for CO from the spectra at low $E_{THz}$ and observed a significant peak broadening with increasing $E_{THz}$ (see section VI in the Supporting Information for a detailed discussion of peak broadening). We further extracted $V_{THz}$ by numerically fitting each THz-RS spectrum with the THz-free IETS spectrum obtained at the same tunneling set point and tip position (see details of the fitting process in section V in the Supporting Information). The fitted THz-RS curves closely follow measured data, and the fitted $V_{THz}$ values vary as the Rx photocurrent on the PCA voltage used for THz generation (Figure 3b). The linear fit of $V_{THz}$ against Rx photocurrent yields a slope larger than that presented in Figure 2c, indicating a greater near-field enhancement in the junction likely due to the different THz beam alignment for THz-RS (Figure 3c).
The THz rectification intensity for the CO HR peak increases monotonically with the THz intensity (Figure 3d). Simulation of the HR peak signal as a function of $V_{THz}$ indicates a quadratic dependence for small values of $V_{THz}$ (i.e., <5 mV), accounting for the nonlinear trend as the Rx photocurrent approaches zero (see details of the simulation in section VII in the Supporting Information). Such sensitivity of a molecular vibration on THz far-field intensity suggests a promising application in single-molecule THz sensing through rectification measurement.

Figure 4 displays THz RS spectra and IETS spectra of various molecular species on different metal substrates. For different tip–substrate configurations (Figure 4a–d), THz-RS spectra (Figure 4i–l) obtained at 0.400 THz and the corresponding IETS spectra (Figure 4q–t) exhibited almost identical line shapes and peak positions for CO HR and HT modes. Similar results were obtained for a nickelocene (NiCp$_2$) molecule (Figure 4m,u) and a monodeuterated acetylene (C$_2$HD) molecule (Figure 4n,v) on Cu(001). On the other hand, we found that THz-RS spectral line shapes deviated from the corresponding IETS spectra for pyrrolidine (C$_4$H$_9$N) and hydrogen (H$_2$) (Figure 4o,w,p,x). While all peaks in the THz-RS spectra showed a symmetrical profile, the peaks in IETS spectra appeared as an asymmetrical peak-dip shape. Rectification spectra obtained with chopped sinusoidal bias modulation showed that the peak profile gradually evolved from asymmetrical to symmetrical line shapes as the modulation frequency increased from 10 kHz to 1 MHz, while no significant changes in line shape were observed for modulation frequencies above 1 MHz (see details in section VIII in the Supporting Information). This suggests that the line shape differences between THz-RS and IETS are likely due to the frequency response of the bias modulation in the sub-MHz range, instead of the resonant excitation in the THz frequency range.

We can qualitatively understand such frequency-dependent line shape changes with the following analysis. Both pyrrolidine and hydrogen in a tunneling junction exhibit two-level conductance switching. The potential energy along the switching coordinate can be modeled as an asymmetric double-well potential. The THz-RS spectra showed a symmetrical profile, while the IETS spectra appeared as an asymmetrical peak-dip shape. This suggests that the line shape differences between THz-RS and IETS are likely due to the frequency response of the bias modulation in the sub-MHz range, instead of the resonant excitation in the THz frequency range.

The THz rectification intensity for the CO HR peak increases monotonically with the THz intensity (Figure 3d). Simulation of the HR peak signal as a function of $V_{THz}$ indicates a quadratic dependence for small values of $V_{THz}$ (i.e., <5 mV), accounting for the nonlinear trend as the Rx photocurrent approaches zero (see details of the simulation in section VII in the Supporting Information). Such sensitivity of a molecular vibration on THz far-field intensity suggests a promising application in single-molecule THz sensing through rectification measurement.

**Figure 4.** THz rectification spectroscopy (RS) and inelastic electron tunneling spectroscopy (IETS) for various molecules. (a–h) Constant-current topographies of different tip/molecule/substrate systems with red stars (★) indicating the tip position selected for spectral acquisition near the center of each molecular image. The corresponding THz-RS spectra ((i–p)) and IETS spectra ((q–x)) are displayed below each topography. The spectra shown in (i), (q), (l), (t), (n), and (v) were background subtracted to remove features from the metal substrate (see section IX in the Supporting Information). For THz-RS spectra, a square wave chopping frequency of 273 Hz was used for (i–o) and 255.11 Hz for (p); for each corresponding IETS, we applied a sinusoidal bias modulation of the same frequency used for THz chopping in RS. All spectra were measured with a 100 ms lock-in time constant. Other measurement conditions used for topography imaging, THz-RS, and IETS are given in Table S1.
probability of the corresponding switching process will be suppressed. Because of the asymmetry of the double-well potential, increasing the modulation frequency can gradually shift the state population of the molecule toward one of the conductance states, changing the total conductance and therefore the line shape of the rectification spectra. Such a line shape change saturates when the modulation frequency far exceeds the switching rates in both directions, which explains the similar line shapes between THz-RS and MHz-RS. The frequency-dependent change in rectification signal suggests its high sensitivity to the dynamic response of switching systems. Therefore, the THz-induced fast oscillating near field in the tunneling junction can be potentially used to study the atomic-scale switching dynamics in the sub-THz frequency range.

In conclusion, CW THz radiation can induce an effective sinusoidal bias modulation in the STM junction and generate a rectification current that reveals the $I-V$ nonlinearity of the junction. The THz-induced bias modulation amplitude is proportional to its far-field amplitude and sensitive to the THz beam alignment to the STM junction but insensitive to tip–substrate gap variation within the regime of quasi-static approximation. Our results demonstrate the sensitivity of THz rectification to THz power, inelastic electron tunneling-induced molecular excitations, and molecular dynamics.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.nanolett.3c00271](https://pubs.acs.org/doi/10.1021/acs.nanolett.3c00271).

Tip and sample preparation, focusing and aligning a THz beam into an STM junction, ambient detection of THz beam position, estimation of tip–substrate gap, fitting THz-RS based on THz-free IETS, THz-induced peak broadening in rectification spectra, simulation of THz-RS peak amplitude as a function of $V_{THz}$, low-frequency AC rectification spectra for hydrogen and pyrrolidine, and background subtraction of spectra (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Office of Naval Research under Grant No. N00014-20-1-2475. We also benefitted from valuable discussions with Jiang Yao, Likun Wang, and Yunpeng Xia.

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