Tip-Enhanced Stokes–Anti-Stokes Scattering from Carbyne

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ABSTRACT: Carbyne, a linear chain of carbon atoms, is the truly one-dimensional allotrope of carbon and the strongest known Raman scatterer. Here, we use tip-enhanced Raman scattering (TERS) to further enhance the Raman response of a single carbyne chain confined inside a double-walled carbon nanotube. We observe an increase of the anti-Stokes scattering by a factor of 3290 and a 22-fold enhancement of the anti-Stokes/Stokes ratio relative to far-field measurements. The power dependence of the anti-Stokes/Stokes ratio under TERS conditions is indicative of coherent Stokes–anti-Stokes scattering mediated by an excited phonon. The role of resonance effects and laser-induced heating are discussed and potential opportunities are outlined.

KEYWORDS: Raman scattering, carbyne, carbon chain, TERS, anti-Stokes

INTRODUCTION

The Raman effect describes the inelastic scattering of light by quantized vibrational excitations (phonons) in matter.1 In the Stokes process, an incoming photon of energy \( h\omega_h \) creates a phonon of energy \( h\omega_S = h\omega_h - h\omega_p \), where \( h \) is the Planck constant and \( \omega \) denotes frequency. On the other hand, in the anti-Stokes process a phonon is annihiliated and the scattered photon is blueshifted to an energy \( h\omega_{S} = h\omega_L + h\omega_p \). Requiring the previous existence of a phonon in the system, the intensity of anti-Stokes scattering is proportional to the phonon occupation number \( n \) described by Bose–Einstein statistics,

\[
\langle n \rangle = \{ \exp[\hbar \omega_p / (k_B T)] - 1 \}^{-1},
\]

where \( k_B \) is the Boltzmann constant and \( T \) is the temperature. In contrast, Stokes scattering can also occur in the absence of a phonon, rendering the Stokes intensity proportional to \( n + 1 \).2 Taking into account the \( \omega^4 \) dependence of Raman scattering, a result of classical field theory, the anti-Stokes/Stokes intensity ratio can thus be written as

\[
\frac{I_{S}}{I_{S}} = \frac{\omega_{S}^{4}}{\omega_{S}^{4}} \times \exp \left[ -\frac{h\omega_p}{k_B T} \right].
\] (1)

Because of the temperature dependence of eq 1, the anti-Stokes/Stokes ratio can be used for calibration-free thermometry.2,5,6 However, there have been many reports of anti-Stokes/Stokes ratios deviating from this simple relation, for instance, in carbon nanotubes7–9 or transition metal dichalcogenides.10 Such anomalous anti-Stokes/Stokes ratios are often related to material resonances, that is, an electronic transition matching the energy of Raman-scattered phonons.7,11,12 Alternatively, the same effect can also be induced by the presence of an external optical resonance, such as a cavity13 or a plasmon.14,15

Another manifestation of the same effect can be seen in the field enhancement.
anti-Stokes signals scale linearly with excitation power (in the absence of laser heating) and the anti-Stokes/Stokes ratio remains constant. On the other hand, in the SaS regime the anti-Stokes scattering intensity assumes a quadratic dependence and, consequently, the anti-Stokes/Stokes ratio increases linearly with laser power. Such nonlinear anti-Stokes scattering intensities have been demonstrated for diamond using high-power ultrafast laser pulses,17 in twisted bilayer graphene tuned into resonance with the anti-Stokes emission,19 and for molecules under surface-enhanced Raman scattering (SERS) conditions.20−22

The motivation for investigating SaS scattering stems from its potential as a source of entangled photons as well as possible applications in quantum information.16−19,23,24 Candidate materials should host phonons with a large energy that are unlikely to be populated at room temperature. Moreover, a large Raman scattering cross section is beneficial to reduce the threshold in terms of local excitation power for the onset of the SaS phenomenon. A material which fulfills these requirements is carbyne, a long chain of sp-hybridized carbon atoms, which represents the truly one-dimensional allotrope of carbon.25,26 The only Raman-active mode of carbyne, termed C-mode, is characterized by a phonon energy of around 1800 cm−1 (ℏωC ≈ 9kBT at 293 K) and a Raman cross section per atom that exceeds that of any other known material by 2 orders of magnitude or more.27

Here, we combine the large phonon energy and Raman cross section of a carbyne chain confined inside a double-walled carbon nanotube with the strong local field enhancement afforded by tip-enhanced Raman scattering (TERS). We observe an anti-Stokes/Stokes ratio that is more than 2 orders of magnitude larger than expected based on thermal phonon statistics. Furthermore, the dependence of the anti-Stokes/Stokes ratio on excitation power suggests that the Stokes and anti-Stokes photons are correlated. Our work thus establishes tip-enhanced Raman scattering of carbyne as a potential source of entangled photon pairs and extends the observation of the SaS effect to one-dimensional systems.

■ RESULTS AND DISCUSSION

Carbyne chains are grown inside double-walled carbon nanotubes following the procedure reported by Shi et al.28 and dispersed on a thin glass coverslip using the recipe described in ref 29. To identify an individual confined carbyne chain (see Figure 1), we capitalize on the nanoscale imaging capabilities of TERS, as described in Methods.

Figure 2 shows the Raman spectrum of a single confined carbyne chain. The spectrum in Figure 2a represents a conventional far-field Raman measurement, while the spectrum in Figure 2b was recorded by TERS. The peaks at ±1834 cm−1 correspond to the C-mode of the carbyne chain, while the feature just below 1600 cm−1 is the G-mode signature of the encasing carbon nanotube structure, likely a bundle of double-walled tubes judging from the topography map in Figure 1b. A small D-peak is visible above 1300 cm−1, indicating the presence of some defects in the nanotubes.11

Looking at Figure 2b, it is striking that the Stokes and anti-Stokes signal strengths are within the same order of magnitude. This observation violates the usual intuition from thermal phonon statistics as expressed by eq 1. To understand the extent to which this large anti-Stokes/Stokes ratio can be attributed to the presence of the TERS tip, let us first discuss the far-field reference measurement depicted in Figure 2a. We fit both Stokes and anti-Stokes peaks with a Lorentzian and obtain the corresponding Raman signals IΣ and IΔ by integration. Taking into account the frequency-dependent response of our setup (see Supporting Information), we find that the experimental far-field anti-Stokes/Stokes ratio amounts to IΔ/IΣ = 3.4 × 10−3. On the other hand, eq 1 at room temperature (293 K) predicts a value of IΔ/IΣ = 2.4 × 10−4, where we have considered that one order of magnitude cancels because we are counting photons rather than measuring intensities.20 Hence, there is a factor of 14 discrepancy between calculated and experimental anti-Stokes/Stokes ratio. This discrepancy can be decomposed into two separate
contributions, a material resonance and heating by the laser. To disentangle those two effects, we record power-dependent far-field measurements to extract the rate of laser-induced heating (see Supporting Information). We find that laser irradiation using 0.65 mW excitation power increases the local temperature to 310 K, thus increasing the anti-Stokes/Stokes ratio by a factor of 1.6 compared to room temperature. The remaining factor of 9 that the experimental anti-Stokes/Stokes ratio deviates from eq 1 we ascribe to a resonance effect. This assignment can be understood by considering the band gap energy of the investigated carbyne chain. It is well-established that for confined carbyne, the band gap energy is linearly related to the C-mode frequency and dictated by the diameter of the encasing inner nanotube.\textsuperscript{5,13,14} On the basis of the Raman shift of 1834 cm\textsuperscript{-1} observed in Figure 2a, we can calculate a band gap energy of 2.1 eV, which is larger than the excitation energy of 1.96 eV. As a consequence, a larger enhancement of the anti-Stokes scattering is expected due to the resonance Raman effect compared to Stokes scattering.\textsuperscript{5,11,12}

Having evaluated the separate contributions of thermal and resonance effects on the far-field anti-Stokes/Stokes ratio, we now focus on the spectrum depicted in Figure 2b, which was acquired in the presence of the TERS tip. Relative to the far-field measurement in Figure 2a, a marked tip-induced enhancement of the Raman response is apparent. The C-mode Stokes peak is enhanced by a factor of 150, mediated by the large field enhancement provided by the used TERS probe geometry (see Methods). The enhancement of the anti-Stokes signal is even more pronounced, amounting to 3290, which implies a 22-fold increase of the anti-Stokes/Stokes ratio by the TERS tip.

We investigate the origin of this tip-induced enhancement of the anti-Stokes/Stokes ratio by performing power-dependent TERS measurements (see Methods). In Figure 3, we plot the measured tip-enhanced anti-Stokes/Stokes ratio $I_{\text{aS}}/I_{\text{S}}$ as a function of laser power $P_L$. To exclude a corruption of the results by the TERS tip drifting away from the laser focus and the carbyne chain, the same measurement series is performed twice in a row. The data points represent the mean values of these measurements. The indicated standard deviations are small (below 5%), suggesting that the validity of our data is not affected by tip drift. Along with the data we plot fits of two different models. The solid black line is a fit of eq 1 with a power-dependent temperature, $T = 293 K + C_T P_L$, and an additional resonance factor $R$

$$\frac{I_{\text{aS}}}{I_{\text{S}}} = R \times \frac{\omega_{\text{aS}}^3}{\omega_{\text{S}}^3} \times \exp \left[ -\frac{-\hbar \omega_{\text{ph}}}{k_{\text{B}} (293 K + C_T P_L)} \right].$$ (2)

Note that compared to eq 1, we have now explicitly replaced the $(\omega_{\text{aS}}/\omega_{\text{S}})^3$ term by $(\omega_{\text{aS}}/\omega_{\text{S}})$ in order for $I_{\text{aS}}/I_{\text{S}}$ to reflect the ratio of anti-Stokes and Stokes photons rather than intensities.\textsuperscript{2,30} The resonance factor $R$ is set to its experimentally determined value of 9, extracted from the far-field data in Figure 2a. In doing so, we are implying that R is not affected by the TERS tip. This assumption is justified because the plasmonic resonance of the tip is engineered such that the field enhancement is equivalent at the Stokes and anti-Stokes frequencies, as elaborated in Methods. Thus, the only free fitting parameter is the rate of laser-induced heating $C_T$ in the presence of the tip. For the fit represented by the red dashed line, an additional term linear in laser power is included in the model

$$\frac{I_{\text{aS}}}{I_{\text{S}}} = R \times \frac{\omega_{\text{aS}}^3}{\omega_{\text{S}}^3} \times \left\{ \exp \left[ -\frac{-\hbar \omega_{\text{ph}}}{k_{\text{B}} (293 K + C_T P_L)} \right] + C_{\text{SaS}} P_L \right\}.$$ (3)

The coefficient $C_{\text{SaS}}$ describes the anti-Stokes signal arising from Stokes-induced anti-Stokes scattering, that is, it accounts for the correlated $\text{SaS}$ process. Equation 3 is an approximation, which is generally valid for high-frequency phonons.\textsuperscript{24,33} While the coefficient $C_{\text{SaS}}$ can in principle be expressed in terms of fundamental constants, such as coupling and decay rates,\textsuperscript{24} it is used here as a phenomenological fitting parameter. The assumption that the local temperature increases linearly with laser power implied in eqs 2 and 3 is discussed in Supporting Information.

Looking at the fit of eq 2 in Figure 3, it is apparent that the exponential Boltzmann factor with a power-dependent temperature alone fails to reproduce the evolution of the anti-Stokes/Stokes ratio with laser power. Moreover, the heating rate $C_T$ returned by this fit amounts to 316 K/mW, which appears unphysical given that the heating rate experimentally determined from the far-field measurements is an order of magnitude lower (see Supporting Information). Further evidence that speaks against such pronounced heating is given by the nanotube G-mode signature, as also detailed in the Supporting Information.

Let us now consider the fit of eq 3 (red dashed line in Figure 3), which allows for the possibility of correlated $\text{SaS}$ scattering. We observe an excellent agreement of this fit with the experimental data. The fitted coefficient $C_{\text{SaS}}$ is a measure of the significance of the $\text{SaS}$ process, amounts to $6.3 \times 10^{-3}$ mW\textsuperscript{-1}, while the returned heating rate $C_T$ is close to zero. We emphasize that this does not imply that there is no heating at all, because assuming a heating rate of several tens of K/mW does not notably compromise the quality of the fit. However, it is clear that the fit of eq 3 is dominated by the $\text{SaS}$ term and that this fit captures the evolution of the anti-Stokes/Stokes ratio with laser power much better than the purely thermal model. Importantly, it is only under TERS conditions that we observe this effect. In power-dependent far-field measurements, no significant contribution of $\text{SaS}$ scattering is apparent.
In summary, we have reported an anomalously large anti-Stokes/Stokes ratio in the tip-enhanced Raman spectrum of confined carbyne. This observation is in part due to the generation of correlated SaS photon pairs, as evident from the linear excitation power dependence of the anti-Stokes/Stokes ratio under TERS conditions. Another sizable contribution to the measured anti-Stokes/Stokes ratio arises from the occurring SaS phenomenon in any material. This is exemplified by the absence of a notable anti-Stokes G-peak in Figure 2b, which indicates that for the carbon nanotubes no significant SaS scattering is occurring. Similarly, for graphene, we observe that the TERS tip increases the G-mode anti-Stokes/Stokes ratio only by a factor of 3.1 (see Supporting Information), in stark contrast to the 22-fold enhancement measured for carbyne. The fact that SaS scattering, under identical TERS conditions, only occurs for carbyne and not for other carbon nanomaterials clearly highlights that the SaS phenomenon is related to the intrinsic properties of carbyne. Specifically, it is the high phonon energy and the large Raman scattering cross section of carbyne that provide a much lower threshold in terms of local excitation power for the onset of SaS scattering compared to other materials.

Finally, let us briefly contrast TERS, which is used in our experiments to transition the Raman scattering of carbyne into the SaS regime, with SERS, which in principle is able to provide similar conditions with even stronger local field enhancements. A shortcoming of commonly used SERS substrates such as roughened metal surfaces or colloidal aggregates is that they give rise to spectra of limited reproducibility regarding intensity and appearance. These limitations originate from the heterogeneity of the plasmonic resonances present on the substrate as well as the stochastic placement of individual sample molecules with respect to local electromagnetic hotspots. On the other hand, TERS probes like the one used in this study can be fabricated with a high degree of reproducibility and a precisely tuned plasmonic resonance behavior (see Methods). Moreover, the positioning of the TERS tip and the associated field intensity hotspot relative to the sample can be precisely controlled. Lastly, direct contact between sample and plasmonic nanostructure is avoided in TERS but standard in typical SERS experiments. This direct contact with the metal can affect the electronic structure of the sample and thus alter the resonance conditions in an unpredictable way. To summarize, TERS provides a level of control that SERS cannot offer, which is of particular importance for reproducible single-molecule studies as performed in the present work.

**CONCLUSION AND OUTLOOK**

In summary, we have reported an anomalously large anti-Stokes/Stokes ratio in the tip-enhanced Raman spectrum of confined carbyne. This observation is in part due to the generation of correlated SaS photon pairs, as evident from the linear excitation power dependence of the anti-Stokes/Stokes ratio under TERS conditions. Another sizable contribution to the measured anti-Stokes/Stokes ratio arises from the resonance Raman effect enhancing the anti-Stokes emission more efficiently than the Stokes emission, which we have demonstrated using far-field data as a reference.

From the theory of resonance Raman scattering in solids, the anti-Stokes emission is expected to be largest when in resonance with an electronic transition, that is, for excitation energies that are lower than the band gap energy by exactly the energy of the phonon that is annihilated in the anti-Stokes process. In the present study, the investigated carbyne chain has a phonon energy of roughly 230 meV and a band gap of 2.1 eV. Hence, the excitation energy of 1.96 eV used in our experiments presumably does not fully exploit the potential of the Raman resonance effect in enhancing the anti-Stokes/Stokes ratio. Optimizing the resonance conditions can increase the efficiency of the SaS process, as demonstrated for twisted bilayer graphene. Moreover, a recent theoretical study suggests that the correlations between Stokes and anti-Stokes photons can be enhanced by modifying the statistical properties of the incident light.

In terms of potential applications, SaS scattering has been investigated as a write-read protocol for solid state quantum memory, where a Stokes-induced phonon stores information that can be read out by an anti-Stokes process during the lifetime of the phonon. In our experiments, the transition of the Raman scattering from carbyne into the SaS regime is mediated by the plasmonic field enhancement afforded by a TERS probe. While TERS is an arguably nontrivial experimental technique compared to SERS, it allows for a precise tuning of the scattering enhancement by varying the tip–sample distance. Thereby, the correlated character of the SaS photons can potentially be tuned continuously from classical to quantum.

**METHODS**

**TERS Measurements.** Our home-built TERS setup is based on an inverted optical microscope with a scanning probe microscope on top. A radially polarized laser beam (excitation energy 1.96 eV) is strongly focused by a high numerical aperture oil-immersion objective. Positioning a TERS probe into the laser focus generates a nanoscale excitation source for Raman scattering. The TERS probe is attached to a piezoelectric tuning fork and its distance from the sample surface is controlled by a shear-force feedback system. The backscattered light is collected in the same objective lens and analyzed by a CCD-equipped spectrometer after passing a notch filter that removes the Rayleigh component. A motorized neutral density filter wheel placed in the beam path allows for varying the excitation power while the TERS probe is engaged. All power values reported in this work were measured before the back aperture of the objective. For imaging, the spectral region of carbyne’s C-mode Stokes peak is isolated by a narrow band-pass filter and detected by an avalanche photodiode while the sample is raster-scanned with a piezo stage. Optical and topographic information is acquired simultaneously (see Figure 1). The integration times are 25 ms/pixel for imaging and 5 s for full TERS spectra (up to 900 s for far-field spectra). An illustration of our TERS setup is provided in the Supporting Information. More details about the principles and experimental implementation of TERS can be found in ref 39.

**TERS Probe.** In this work we employ a plasmon-tunable tip pyramid (PTTP) made from gold as TERS probe. This probe geometry consists of a micropyramidal frustum with a...
nanopyramidal end. The size of the nanopyramid is set by the fabrication process to 470 nm, such that the tip supports a localized surface plasmon resonance monopolar mode at the excitation wavelength of our laser.\textsuperscript{40–42} As a consequence, the PTTP probe provides a stronger field enhancement at its apex compared to regular gold micropyramids,\textsuperscript{43} resulting in the large signal enhancement observed in Figure 2. Importantly, the plasmonic resonance of the PTTP probe is not only centered by design at the excitation energy of our laser but is also symmetric to within 0.3 eV from the resonance peak maximum.\textsuperscript{40,41} Equal field enhancement can therefore be expected at the Stokes and anti-Stokes frequencies of carbonyl. Consequently, the resonance factor R in eqs 2 and 3 does not differ from its far-field value obtained from Figure 2a. The plasmonic spectral shaping effect,\textsuperscript{39,44} which typically needs to be considered when evaluating anti-Stokes/Stokes ratios in plasmon-enhanced spectroscopy, does therefore not play a role in the TERS experiments presented in this work.

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