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Raman Scattering Cross Section of Confined Carbyne

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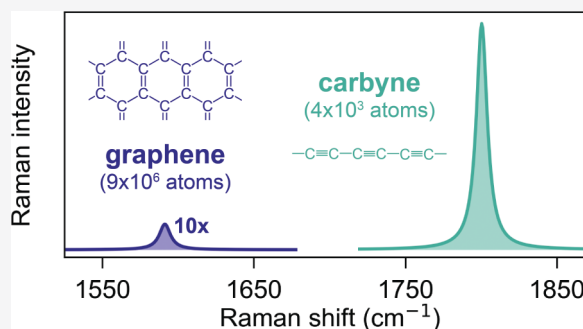
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ABSTRACT: We experimentally quantify the Raman scattering from individual carbyne chains confined in double-walled carbon nanotubes. We find that the resonant differential Raman cross section of confined carbyne is on the order of 10^{-22} $\text{cm}^2 \text{sr}^{-1}$ per atom, making it the strongest Raman scatterer ever reported.



KEYWORDS: carbyne, linear carbon chains, Raman scattering, Raman scattering cross section, TERS

INTRODUCTION

Carbyne, an infinitely long linear chain of carbon atoms, is the paradigmatic sp -hybridized and truly one-dimensional allotropic form of carbon.^{1,2} Because of a Peierls distortion, the equilibrium structure of carbyne is polyynic with alternating single and triple bonds, as shown in Figure 1a, and therefore characterized by a dimerized (biatomic) unit cell. As a consequence, polyynic carbyne is a direct band gap semiconductor and has one Raman active phonon mode, termed C-mode, which corresponds to an in-phase stretching of the triple bonds along the chain.^{3,4}

Attempts to synthesize carbyne have long been limited by its extreme chemical instability.⁵ This obstacle has been overcome by growing carbon chains inside carbon nanotubes, which act as nanoreactors and shield the chains from interaction with the environment.^{6–13} Lengths up to several thousand atoms have been reported for linear carbon chains synthesized inside double-walled carbon nanotubes (DWCNTs).¹⁴ In contrast to short chains comprising few or few tens of atoms,^{13,15–17} the properties of these long chains do not exhibit any length-dependence, indicating that they are the finite realization of carbyne.¹⁸

As for other carbon nanostructures,^{19–22} Raman spectroscopy is a powerful tool to study the vibrational and electronic properties of carbyne. For carbyne chains encapsulated inside DWCNTs, the C-mode Raman shift and the carbyne band gap energy E_{gap} are both linearly related to the diameter of the enclosing inner nanotube and therefore tunable by choice of nanotube host.¹⁸ Moreover, strong resonant enhancement of the C-mode Raman signal occurs for excitation energies E_L in the neighborhood of E_{gap} .^{13,23}

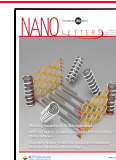
While Raman scattering is in general a weak effect, strong Raman intensities are predicted by effective conjugation coordinate theory for collective oscillations along the molecular backbone of π -conjugated systems characterized by a bond-alternation pattern.^{24–26} For carbyne, this is supported by the fact that even short chains comprising a mere few hundred atoms can be readily detected with conventional Raman spectroscopy. Quantifying the Raman cross section of carbyne is therefore of significant interest due to its anticipated large magnitude and will enable Raman spectroscopy to be used as a simple yet effective method to evaluate the currently unknown yield of carbyne synthesis directly from far-field bulk measurements.¹⁴ Besides, absolute cross sections for Raman scattering can serve as a stringent test to the theories used to describe the scattering mechanism, and it is customary to deduce from these absolute values quantitative results about other core material properties such as electron–phonon coupling constants.^{27,28} Yet, to date the absolute magnitude of the Raman response of carbyne has remained unexplored.

In this Letter, we experimentally quantify the Raman scattering from confined carbyne. We find that the resonant differential Raman cross section of confined carbyne is on the order of 10^{-22} $\text{cm}^2 \text{sr}^{-1}$ per atom, exceeding that of any other known material by 2 orders of magnitude or more. Our results

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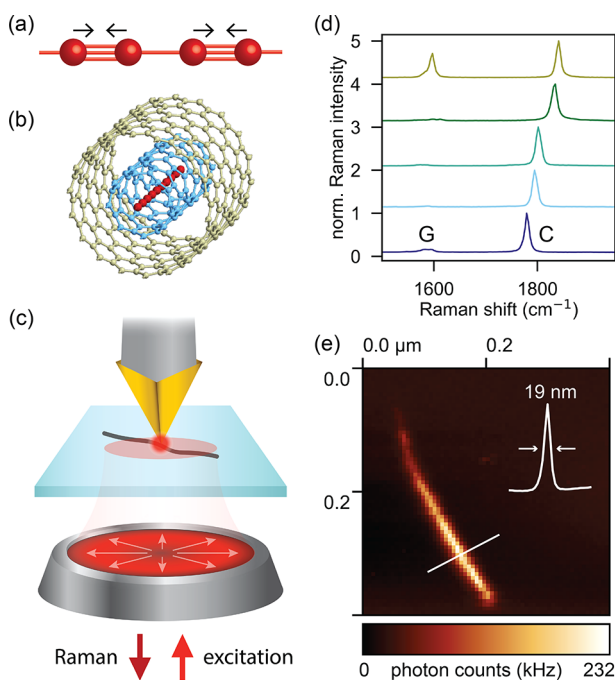


Figure 1. (a) Atomic structure of polyyne carbyne. Arrows indicate atomic displacements for the Raman-active C-mode. (b) Carbyne chain encapsulated inside a double-walled carbon nanotube (DWCNT). (c) Schematic illustration of our TERS setup. (d) TERS spectra of confined carbyne. The G-peaks arise from the DWCNT. The spectra are vertically offset for better visibility and normalized to the height of the respective C-peak. (e) TERS image of the C-mode of a confined carbyne chain. The intensity profile (inset) extracted along the white line shows a spatial resolution of 19 nm.

therefore establish confined carbyne as the strongest Raman scatterer ever reported.

EXPERIMENTAL SECTION

Carbyne chains are grown inside DWCNTs in a high-temperature, high-vacuum process as described in ref 14 and dispersed on a thin glass coverslip. Our strategy to quantify the resonant differential Raman cross section of confined carbyne then comprises the following steps. First, we identify individual chains by tip-enhanced Raman spectroscopy (TERS) and extract their length for later normalization. Second, we perform far-field Raman measurements with a tunable excitation source to excite each carbyne chain on resonance. Finally, we obtain the absolute differential Raman cross section of carbyne by comparison to a reference scatterer.

In the first characterization step, we perform TERS using a home-built setup,^{29,30} schematically illustrated in Figure 1c. A radially polarized laser beam (excitation energy 1.96 eV), tightly focused by a high numerical aperture (NA 1.4) oil-immersion objective, generates a nanoscale excitation source at the apex of an optical nanoantenna.³¹ The antenna is attached to a piezoelectric tuning fork and positioned in close proximity to the sample surface with a shear-force feedback system. The backscattered light is detected either by an avalanche photodiode (APD) or a CCD-equipped spectrometer. In the first case (detection by the APD), the scattered beam passes through a narrow band-pass filter that transmits only the spectral region of carbyne's C-mode. Images are formed by raster-scanning.

We consider in this work a total of 20 different confined carbyne chains. For each individual chain, we record a TERS

spectrum and a TERS image from which we obtain the C-mode frequency and the chain length, respectively. Representative measurements, recorded with a power of $\sim 100 \mu\text{W}$ before the back aperture of the objective, are displayed in Figure 1d,e. An overview of all the extracted chain lengths l_C and C-mode frequencies is given in Figure 2a. No dependence of the C-mode frequency on chain length is evident, indicating that the confined carbon chains are indeed the finite realization of carbyne. In addition, we indicate in Figure 2a the band gap energy E_{gap} for every carbyne chain, which can be directly inferred from the corresponding C-mode frequency.¹³ The lack of C-mode frequencies between 1808 and 1823 cm^{-1} , highlighted by the gray area, is in agreement with other works^{6–14,18} and can be interpreted in the context of the linear relation between inner nanotube diameter and C-mode frequency of the encapsulated carbyne chain reported in ref 18. According to this model, only the metallic (9,0) and (8,2) nanotubes fall in the diameter range for which the corresponding C-mode frequencies are not observed. The reason for this apparent lack of polyyne carbyne inside metallic host nanotubes remains unclear to date. As discussed in ref 18, the growth process of carbyne could be less efficient inside metallic nanotubes compared to semiconducting ones. Alternatively, the interaction between carbyne and the encapsulating host nanotube might differ for metallic and semiconducting tubes, resulting in C-mode frequencies deviating from the linear trend established in ref 18.

In the second step of our characterization approach, we carry out resonant far-field Raman measurements on the previously identified carbyne chains. We employ a backscattering geometry with an air objective (NA 0.9) and polarized detection parallel to the polarization of the excitation laser (for details, see ref 23). A dye laser serves as tunable excitation source. For every carbyne chain, the excitation energy E_L is chosen to closely match the band gap E_{gap} to ensure maximum resonance enhancement of the Raman intensity ($|E_L - E_{\text{gap}}|$ below 20 meV and thus small compared to the line width of the resonance)²³. The linear polarization of the excitation beam is adjusted for every measurement to coincide with the chain axis. This takes into account that for one-dimensional systems, owing to their anisotropic polarizability, Raman scattering arises only from the projection of the incoming light onto the system's main axis.^{19,23}

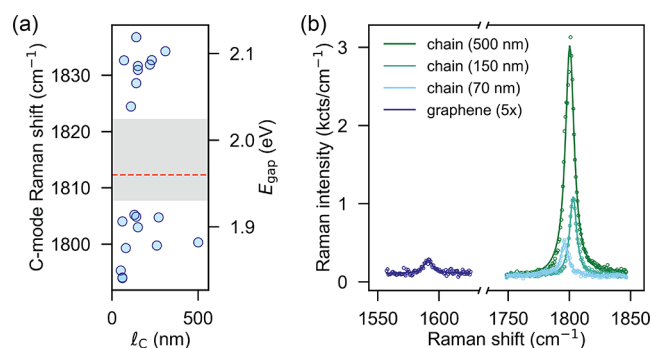


Figure 2. (a) C-mode Raman shift, band gap energy E_{gap} , and length l_C of 20 confined carbyne chains characterized by TERS. The gray area highlights the apparent lack of polyyne carbyne inside metallic host nanotubes (see main text); the dashed line marks the excitation energy (1.96 eV) used for TERS. (b) Far-field Raman spectra of graphene and three carbyne chains of different length, all recorded at 1.89 eV with $\sim 360 \mu\text{W}$ power, and 60 s integration time. The lines represent Lorentzian fits on a linear background.

Figure 2b shows the Raman spectra of three different carbyne chains excited close to resonance with excitation energy 1.89 eV. We fit each spectrum with a Lorentzian on a linear background. The integrated C-peak intensities obtained from the fits represent the corresponding resonant Raman signal A_C for every chain. We observe that the Raman signal increases linearly with chain length. To extend this finding to carbyne chains with different band gaps, measurements carried out at different excitation energies need to be compared. For this, it is essential to take into account the pronounced wavelength-dependence of the detection system response.

In our final characterization step, we compare the resonant Raman signals of carbyne chains with different band gap energies and calibrate the signal strength. To this end, we employ the method of sample substitution.^{27,28} This consists in normalizing the Raman signal of each individual carbyne chain to that of a substitutional scatterer, for which the absolute differential Raman cross section as a function of excitation energy is known. Here, we choose as a reference the integrated G-peak intensity of graphene, A_G (see Figure 2b). We mechanically exfoliate graphene directly onto a glass substrate and identify a monolayer region that is much larger than the laser spot size using hyperspectral Raman mapping (see Supporting Information). After every (near-)resonant measurement of a carbyne chain, we acquire the Raman spectrum of graphene using the exact same experimental configuration. In this way, the ratio A_C/A_G of the corresponding signals is deconvolved from the wavelength-dependent response of the detection system. Note that for any given excitation energy we neglect the difference in sensitivity of our detection system for the C-mode of carbyne and the G-mode of graphene. This is only justified because the two modes have very similar Raman frequencies. The laser power before the back aperture of the objective is kept below 400 μ W to avoid sample heating.

RESULTS AND DISCUSSION

The combined results from TERS and resonant far-field Raman measurements on 20 isolated confined carbyne chains are displayed in Figure 3a. We find that the resonant Raman signal A_C of carbyne, normalized by the G-peak Raman signal A_G of graphene recorded under the exact same experimental conditions, is proportional to the carbyne chain length l_C .

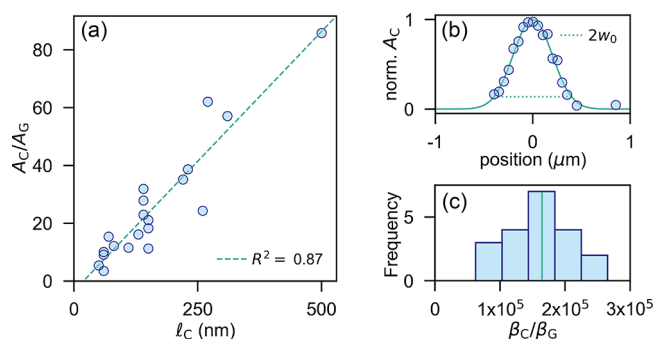


Figure 3. (a) Resonant Raman signal A_C of confined carbyne, normalized by the G-peak Raman signal of graphene A_G , as a function of carbyne chain length l_C . The linear fit (dashed line) is characterized by an R^2 value of 0.87. (b) Profile of the intensity distribution in the focal plane, recorded at 1.84 eV. Gaussian fitting yields a beam waist of $w_0 = 390$ nm. (c) Histogram of the ratio of the differential Raman cross section per atom of carbyne (β_C) and graphene (β_G) for 20 different carbyne chains. The green line marks the median value.

Moreover, for the longest measured carbyne chains, the Raman signal is almost 2 orders of magnitude stronger compared to that of graphene. This result is particularly striking when considering that the number of atoms contributing to the respective signals differs substantially.

Before discussing the magnitude of carbyne's Raman response in more detail, let us first briefly elaborate on the linear length-dependence. As may be observed in Figure 3a, the linear trend does not start exactly at the origin. This is an artifact of the finite TERS resolution, which leads to a slight overestimation of the carbyne chain lengths l_C . Residual deviations from the linear fit arise from finite differences $|E_L - E_{\text{gap}}|$ between excitation and carbyne band gap energies and power fluctuations or drift during the signal acquisition. The linear scaling of the carbyne Raman signal with chain length indicates that the phonon coherence length is negligible compared to the chain length and that Raman emission from carbyne can be regarded as an incoherent process.³⁸ Clearly, however, this proportionality is only valid as long as the chain length does not exceed the focal spot size. We verified that this applies to all carbyne chains considered in this work by measuring the waist of the excitation profile in the focal plane. To do so, we scanned a carbyne chain along the direction perpendicular to its main axis through the focal spot and recorded a Raman spectrum every 50 nm. The beam waist w_0 can then be extracted from a Gaussian fit to the integrated C-mode intensities A_C , as shown in Figure 3b. Extrapolating w_0 to the whole range of excitation energies used for the resonant Raman measurements (1.84–2.11 eV) confirms that even the longest measured carbyne chains displayed in Figure 3a lie well within the focal spot (for more details, see Supporting Information).

We now investigate more closely the magnitude of the Raman response of confined carbyne and how it compares to that of graphene. Since our aim is to quantitatively compare Raman scattering from two materials of different dimensionality, it is instructive to refer to a differential Raman cross section β per atom, which constitutes an intrinsic property irrespective of spatial extent. We therefore normalize the recorded Raman signals of carbyne and graphene depicted in Figure 3a by the corresponding number of atoms N involved in each process. The validity of this approach rests upon the proportionality relation established in Figure 3a. For carbyne, the number of atoms is simply given by the chain length l_C as measured by TERS and the atomic line number density $\lambda_l = 7.8 \text{ nm}^{-1}$ ³⁹ as $N_C = l_C \lambda_l$. Similarly, for graphene, $N_G = A_{\text{eff}} \rho_A$. Here, $\rho_A = 38.2 \text{ nm}^{-2}$ is the atomic surface number density of graphene,^{40,41} and $A_{\text{eff}} = \pi w_0^2 / 2$ denotes the effective surface area of the Gaussian excitation.⁴² Finally, we can calculate the ratio of the differential Raman cross section per atom of carbyne compared to graphene as $\beta_C/\beta_G = (A_C/N_C)/(A_G/N_G)$.

The results are represented by the histogram in Figure 3c for all of the measured carbyne chains. We find that the differential Raman cross section per atom of confined carbyne is 5 orders of magnitude larger than that of graphene. Given that graphene is widely recognized as a strong Raman scatterer,^{20,21} this result clearly demonstrates a giant Raman effect from confined carbyne. Within our experimental precision, we do not observe a systematic dependence of β_C/β_G on C-mode frequency. Hence, unlike other properties¹⁸ the differential Raman cross section β_C of polyynic confined carbyne seems to be largely unaffected by the interaction with the encapsulating nanotube.

Having established a relative value for the differential Raman cross section per atom of confined carbyne, we now focus on

Table 1. Differential Raman Cross Section β of Confined Carbyne Compared to Other Materials and Molecules, Determined at Excitation Energy E_L ^a

	Raman mode (cm ⁻¹)	E_L (eV)	β (cm ² sr ⁻¹)	ref.
Confined carbyne	1793–1837	1.84–2.11	$(0.7–1.1) \times 10^{-22}$	this work
Rhodamine 6G	1504	2.33	$*9.6 \times 10^{-25}$	32
Carbon nanotube	200	1.96	2.7×10^{-25}	33
Graphene	1584	2.41	1.2×10^{-27}	34
Buckminsterfullerene (C ₆₀)	1469	1.65	$*2.1 \times 10^{-29}$	35
Diamond	1332	2.41	3.4×10^{-30}	36
N ₂ gas	2331	2.54	$*3.3 \times 10^{-31}$	37

^aAll values of β refer to one atom (*molecule) *in vacuo*.

turning this into an absolute result. To this end, we make use of the Raman tensor component $|a| = 92 \text{ \AA}^2$ measured for the G-band of graphene at an excitation energy $E_L = 2.41 \text{ eV}$ in ref 34, which translates to a differential Raman cross section per atom of $\beta_G = 1.2 \times 10^{-27} \text{ cm}^2 \text{ sr}^{-1}$,^{27,38,43–45} as shown in the Supporting Information. In order to use this value as a reference, we extrapolate it based on the known E_L^4 -scaling of β_G ^{46,47} to the excitation energies (1.84–2.11 eV) used in this work. Together with the median of $\beta_C/\beta_G = 1.6 \times 10^5$ shown in Figure 3c, we find that the differential Raman cross section of confined carbyne amounts to $\beta_C = (0.7–1.1) \times 10^{-22} \text{ cm}^2 \text{ sr}^{-1}$ per atom. The indicated range for β_C considers the variation in excitation energy used to resonantly excite carbyne chains with different band gap energies, as elaborated in the Supporting Information. The uncertainty of our experimental results, based on the standard deviation of 0.5×10^5 of the data displayed in Figure 3c, is around 30%.

To put our results for the differential Raman cross section per atom of confined carbyne into context, we provide in Table 1 a comparison of differential Raman cross sections reported for other carbon allotropes. In addition, we also include Rhodamine 6G, which is known to have a large resonant Raman cross section, and nitrogen gas (N₂), which features a weak, nonresonant Raman cross section. Inspection of Table 1 underlines that the order of magnitude of the differential Raman cross section of confined carbyne is unprecedented, by far exceeding the reported values for any other material or molecule. We point out that for this comparison to be fair, it is essential to take local field effects into account. The presence of a substrate or solvent modifies the local electromagnetic environment of the sample and thereby affects the measured Raman cross sections.^{34,42,48–51} We thus applied local field corrections to some of the values listed in Table 1, such that they all represent differential Raman cross sections *in vacuo* and are therefore not obscured by the influence of an underlying or surrounding medium (details are given in the Supporting Information).

CONCLUSION AND OUTLOOK

In conclusion, we have demonstrated that confined carbyne is so far the strongest known Raman scatterer with a resonant differential Raman cross section per atom on the order of $10^{-22} \text{ cm}^2 \text{ sr}^{-1}$. Its unrivaled Raman cross section renders carbyne a promising candidate for experiments that rely on strong interaction between light and vibrational modes. For instance, combined with plasmonic⁵⁰ or cavity⁵² enhancement, carbyne may provide a platform for studying vibrational strong coupling,⁵³ hot vibrational transitions,⁵⁴ vibrational pumping,⁵⁵ and molecular quantum optomechanics.⁵⁶ Further, confined carbyne holds great potential as a Raman label for biological

imaging. This is similar to dye molecules encapsulated inside functionalized carbon nanotubes for which such applications have already been demonstrated.⁵⁷ However, confined carbyne not only has a differential Raman cross section that is 2 orders of magnitude larger but provides the additional advantage that band gap energy and Raman frequency can be tuned by choice of host nanotube^{18,58} and that very few other compounds exhibit Raman features in the same spectral region.⁵⁹ Finally, we expect that the quantification of carbyne's Raman cross section provided here will serve as a valuable reference point for theoretical calculations and might start closing the circle into some of the outstanding electronic,⁶⁰ thermal,⁶¹ and mechanical⁶² properties anticipated for carbyne.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.0c02632>.

Hyperspectral Raman imaging of graphene; Effective scattering length for one-dimensional systems; Local field corrections; ω^4 -dependence of Raman scattering; Standardizing Raman scattering cross section values from the literature including additional Raman data of DWCNTs (PDF)

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Notes

The authors declare no competing financial interest.

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