Electron-phonon coupling and vibrational properties of size-selected linear carbon chains by resonance Raman scattering

UV resonance Raman spectroscopy of size-selected linear sp-carbon chains unveils vibrational overtones and combinations up to the fifth order. Thanks to the tunability of the synchrotron source, we excited each H-terminated poly-yne (HCₙH with n = 8,10,12) to the maxima of its vibronic absorption spectrum allowing us to precisely determine the electronic and vibrational structure of the ground and excited states for the main observed vibrational mode. Selected transitions are shown to enhance specifically over orders in the Raman spectrum in a specific way that can be explained by a simple analytical model based on Albrecht’s theory of resonance Raman scattering. The determined Huang–Rhys factors indicate a strong and size-dependent electron-phonon coupling increasing with the sp-carbon chain length.
Resonance Raman spectroscopy has been rarely employed to investigate the vibrational spectra of short sp-carbon systems. Pre-resonance and resonance conditions have been exploited for polyynes absorbing in the UV. Recently resonance Raman in the visible range has been used to infer the excitation profile of confined carbynes. The evaluation of an average Huang–Rhys factor of 1.82 indicates a large electron-phonon coupling and accounts for the extremely high Raman activity of this system. In this framework, the size-dependent resonance Raman behavior and the electron-phonon coupling in the limit of short sp-carbon wires is an open issue.

In this work, we provide a resonance Raman investigation of size-selected H-terminated polyynes, as the simplest model of sp-carbon wires in the short size limit. Such systems represent the simplest linear carbon chain comprising sp-hybridized carbon atoms only and prove to be the ideal system to investigate resonance Raman processes in detail. We exploited synchrotron radiation as a tunable coherent UV light source to precisely excite the size-dependent absorption vibronic transitions (2172 cm\(^{-1}\) of C\(_8\)) and UV resonance Raman spectra of C\(_8\), excited by three different wavelengths: 226 nm (|0\(\rangle\_g\rightarrow |0\rangle\_e\), a), 216 nm (|0\(\rangle\_g\rightarrow |1\rangle\_e\), b), and 206 nm (|0\(\rangle\_g\rightarrow |2\rangle\_e\), c, d). The signals above 6000 cm\(^{-1}\) in all panels are magnified to highlight low-intensity signals. The vibrational lines of the solvent are shadowed by white boxes. The spectra are normalized to the CN stretching peaks of acetonitrile.
bands when exciting in resonance with the first (\(k = 0\)) vibronic transition (226 nm), despite the low concentration of \(\text{C}_8\) (see Supplementary Table 1), while it is much less intense when tuning the synchrotron radiation to 216 nm (\(k = 1\)) and 206 nm (\(k = 2\)) (see Figs. 1 and 2). Moreover, at 226 nm excitation, we observe a satellite peak close to the \(\alpha\) line at 2082 cm\(^{-1}\) (named \(\beta\) line\(^25\)), which is assigned to another CC stretching mode of the sp carbon chain\(^3,23,25\). The intensity of the \(\beta\) line is always lower than that of the \(\alpha\) line, being almost non-detectable at 206 nm (\(k = 2\)).

In the region beyond the OH stretching of water (>4000 cm\(^{-1}\)), resonance Raman spectra of \(\text{C}_8\) at different excitation energies show features located at approximately two, three, four, and five times the Raman shift of the \(\alpha\) and \(\beta\) peaks, immediately ascribed to overtones (\(m\alpha + n\beta\), with \(m\) and \(n\) being the number of vibrational quanta) and combination bands (\(m\alpha + n\beta\))—see Figs. 1 and 2. In particular, the second-order region (4000–4400 cm\(^{-1}\)) shows 3 peaks that correspond to the first overtones and combination of the \(\alpha\) and \(\beta\) lines, namely \(2\alpha\), \(2\beta\), and \(\alpha + \beta\). The three quanta region (6000–6600 cm\(^{-1}\)) allows identifying the expected four overtones and combinations (3\(\alpha\), 2\(\alpha + \beta\), \(\alpha + 2\beta\), 3\(\beta\)). The fourth-order Raman region (8000–8800 cm\(^{-1}\)) shows four of its five distinctive overtones and combinations (4\(\alpha\), 3\(\alpha + \beta\), 2\(\alpha + 2\beta\), \(\alpha + 3\beta\), 4\(\beta\)), only when in resonance with the \(|0\rangle_{g} \rightarrow |2\rangle_{e}\) vibronic transition at 206 nm. Indeed, only weak features, hardly detectable in the background, can be seen when in resonance with the \(|0\rangle_{g} \rightarrow |0\rangle_{e}\) vibronic transition at 226 nm. Such difference is more evident for the fifth-order region where a rather broad band centered at about 10,700 cm\(^{-1}\) is detectable only when exciting at 206 nm (\(k = 2\)) and represents the convolution of the six expected overtones and combinations. In the measured UVRR spectra, we also observe that combination modes with increasing \(\beta\) contribution show decreasing intensities within the same overtone manifold. This is expected because the Raman intensity of the \(\beta\) line is significantly smaller than the intensity of the \(\alpha\) line, and the Raman intensity of combinations can be approximated—in resonance condition—by the product of the intensities of the related fundamental Raman transitions\(^38\).

**Discussion**

The combined use of the experimental UV-Vis absorption and resonance Raman spectra allowed us to investigate the vibrational fine structure of the \(\alpha\) mode in short polyynes. From the resonance Raman spectra recorded at different excitation wavelengths, we have determined the vibrational levels of the ground state of the \(\alpha\) mode up to \(|5\rangle_{g}\) as shown in Fig. 3 for \(\text{C}_8\). The position of each vibrational level is the energy of the fundamental transition of the \(\alpha\) mode and its
shown in Fig. 3 for C8. Similar results are obtained for C10 and C12 (see arrows in Fig. 3). Considering both the ground and the excited states of C8, the energy spacing extracted from experimental excited states of C8, the energy spacing extracted from experimental levels (see arrows in Fig. 3). Considering both the ground and the excited states, respectively. Hence, in the following, we will assume the harmonic approximation for both the ground and excited state potential energy surfaces. Moreover, the spacing between experimentally determined vibrational levels is almost equal in the ground and excited states, e.g., 0.269 eV and 0.253 eV, respectively, for C8 (see Fig. 3). Thus, it is reasonable to adopt the same harmonic approximation of the potential energy surfaces for the ground and excited states. Hence, by the analysis of the clear vibronic progression of polynes, and by the observation of high order Raman features, made possible by the high enhancement and resolution of the SR-based UVRR setup at Elettra, we can precisely assess the vibronic levels of polynes despite the very low concentration of the samples.

In this framework, an important parameter to evaluate the optoelectronic properties of conjugated systems is the strength of the electron-phonon coupling. We can investigate it by calculating the Huang–Rhys (HR) factor, $S$, of polynes. Indeed, in the Franck-Condon model, this nondimensional parameter expresses the average number of quanta involved in the vibrational transition. By keeping the one-mode approximation introduced before, it is possible to quantitatively evaluate the HR factor from the UV-Vis spectrum$^{43}$ Thus, assuming we neglect the effect of higher vibrational levels as initial states in the transition (as discussed above), we can apply the following relation

$$I_0 \propto S^\nu$$

which shows that the $\nu$-th power of the HR factor $S$ is proportional to the ratio of the intensity of the $\nu$-th vibronic transition compared to the fundamental transition. From Eq. (1), we obtain the HR factors for the $\nu=1$ transition of all the H-capped polynes we have discovered so far, i.e., from C8 to C26, whose UV-Vis spectra are reported in Supplementary Fig. 5. The standard deviations reported in Fig. 4 are calculated from the fit errors of the UV-Vis spectra of polynes used to extract the intensity of each vibronic peak.

Within this one-mode model, we can estimate a dimensionless effective displacement parameter ($\delta_{\text{eff}}$), proportional to the distance between the equilibrium position of the ground and excited states. Indeed, the displacement parameter determines both the intensities of the vibronic progressions in UV-Vis absorption spectra and the activities of the collective vibrational modes in Raman spectra of polynes$^{45,46}$. Moreover, it is related to the thermal stability, optoelectronic and quantum chemical properties of molecules. It turns out that the effective displacement parameter is connected to the HR factor of the $\nu=1$ transition (i.e., $S=\delta_{\text{eff}}^2/2$—see Supplementary Discussion$^{14,14}$). In this way, we can directly evaluate the effective displacement parameter (i.e., $\delta_{\text{eff}}=\sqrt{S}$), from the HR factors of all H-capped polynes, as reported in Eq. 4b. In particular, we found $\delta_{\text{eff}}=1.166 \pm 0.04$ for C8 (see also Fig. 3), $1.183 \pm 0.06$ for C10 and $1.225 \pm 0.04$ for C12 (see also Supplementary Fig. 4). Both the HR factors and the effective displacement parameters $\delta_{\text{eff}}$ grow as the length of H-capped polynes increases, showing a strong correlation between the electron-phonon coupling and $\pi$-conjugation in linear sp-carbon chains. The values of the HR factor of H-capped polynes reported in Fig. 4a are larger than those of the radial breathing mode of carbon nanotubes$^{11,19}$, and are comparable with the HR factors found for $\beta$-carotene$^{22,23,41}$. Recently, Martinati et al. calculated the HR factor of long sp-carbon chains ($\approx 100$ carbon atoms) confined in carbon nanotubes from wavelength-dependent resonance Raman measurements and found an average value of 1.82 as a possible upper limit for long chains towards carbyne$^3$. Our results confirm the increasing trend of the HR factor with increasing chain length and $\pi$-conjugation.
In this framework, a two-mode ($\alpha$ and $\beta$) model is required to explain the experimental results, based on Albrecht’s theory of resonance Raman (see Supplementary Discussion) and worked out in the hypothesis of resonance with specific vibronic transitions. The expressions of Raman intensities so obtained require the evaluation of the displacement parameters related to the $\alpha$ and $\beta$ modes, $\delta_1$ and $\delta_2$, respectively. In this way, we can predict the intensity pattern of the $\alpha$ mode and its overtones in the UVRR spectra of polyynes. As illustrated in the Supplementary Discussion, we have determined $\delta_1$ and $\delta_2$ from experimental data by combining the UV-Vis absorption and first-order resonance Raman spectra of each polyyne (see Supplementary Discussion), which resulted in the values of 1.136 and 0.266 for C$_8$, 1.178, and 0.137 for C$_{10}$, and 1.228 and 0.047 for C$_{12}$, respectively. Interestingly, the values of $\delta_1$ ($\alpha$ mode) approach those of $\delta_2$, while $\delta_2$ ($\beta$ mode) goes to zero as the chain length increases, as shown in Fig. 4c. Indeed, the effective displacement parameter is connected to $\delta_1$ and $\delta_2$ according to the relationship $\delta_{\text{eff}} = \frac{\delta_1}{2} + \frac{\delta_2}{2}$ (see Supplementary Discussion). This occurrence makes the one-mode approximation increasingly more reasonable as the length of the chain increases and it is consistent with the expected decrease in the Raman activity of the $\beta$ mode which is ultimately not present in the infinite chain $^{44}$. Based on this observation, we expect that the fine details in the resonance Raman trends are harder to describe with the one-mode approximation in C$_8$ than in C$_{12}$ and longer chains, whose $\delta_2$ is expected to approach zero.

The experimental behavior of the relative Raman intensities of the $m$-th overtones of the $\alpha$ mode ($I_{0,m}/I_{0,1}$) in resonance with different vibronic transitions ($|0\rangle_g \rightarrow |k\rangle_e$) is reported in Fig. 5. The intensity of each $m$th peak has been normalized to that of the fundamental ($m=1$) transition. By exciting C$_8$ at 226 nm ($|0\rangle_g \rightarrow |0\rangle_e$), the intensity ratio follows a decreasing progression vs. the $m$ quantum number of the overtone, as expected in non-resonance Raman scattering. However, by exciting C$_8$ at 216 nm ($|0\rangle_g \rightarrow |1\rangle_e$), the intensity of the second-order (2a) line exceeds that of the first order. Remarkably, at 206 nm ($|0\rangle_g \rightarrow |2\rangle_e$), the relative intensity maximum is reached with the fourth overtone (4a). We also observe a strong modulation of the relative intensities of the $m$th lines for C$_{10}$ and C$_{12}$, as reported in Fig. 5b, c, respectively. By applying Albrecht formalism, we can compute the values of the ratio of the intensity of the $m$th overtone to the first-order mode by the following expression (see Supplementary Discussion):

$$R_{km} = \frac{I_{0,m}}{I_{0,1}} = \frac{1 - \epsilon m \epsilon(k|m)_g}{1 - \epsilon \epsilon(k|1)_g}$$

(2)

where $k$ identifies the specific vibronic resonance ($|0\rangle_g \rightarrow |k\rangle_e$) and $m = 2, 3, \ldots$ labels the first, second, ..., Raman overtone. In Eq. (2) we set $\epsilon = \omega_\alpha / \omega_{\text{uv}}$, where $\omega_\alpha$ and $\omega_{\text{uv}}$ are the quantum energies of the $\alpha$ mode and the UV excitation, respectively (for instance, for C$_8$ at the 226 nm excitation, it is $\epsilon = 0.049$).

In deriving Eq. (2) (see Supplementary Discussion), we have assumed the same harmonic approximation of the potential energy surfaces for the ground and excited states; this choice is justified by the previous analysis of the vibrational structure of the two electronic states. The displacement parameter $\delta_1$ rules the overlap integrals between the vibrational wavefunctions of the ground and excited state (Franck–Condor factors) which appear in Eq. (2), as illustrated in Supplementary Discussion. The relative intensities of the overtones of the $\alpha$ line, obtained by Eq. (2), are reported in Fig. 5. By comparing experimental and theoretical data of Fig. 5, we observe that the model can capture most of the observed modulation of the relative intensities of the overtones for the different resonance conditions, in particular for the $|0\rangle_g \rightarrow |1\rangle_e$ (C$_8$, C$_{10}$, and C$_{12}$)
vibronic transitions. However, in the case of the $|0\rangle_g \rightarrow |2\rangle_e$ resonance condition, the model does not fully account for the observed different behaviors of the three polyynes, and the predicted trends are fairly similar from C8 to C12. This is expected because the adopted assumptions can lose their robustness for Raman transitions involving higher $k$. The analysis of the terms appearing in Eq. (2), allows the rationalization of the observed intensity trends.

Since in Eq. (2) the prefactor containing $\epsilon$ decreases monotonically with $m$, the most relevant term that can account for the non-monotonic behaviors experimentally observed (Fig. 5) depends on the Franck–Condon integrals. For systems with vibronic progressions dominated by the $0$–$0$ and $0$–$1$ transitions, which is typical of systems with a small $\beta$ value close to 1, the overlap between the $k$–$\theta$ and the $m$–$\theta$ vibrational wavefunctions of the electronic excited ($e$) and ground ($g$) state in $\langle k|m \rangle$ is usually significant when $k = m$ and/or $k = m \pm 1$. This explains the remarkable intensity of high-order overtones observed when the experiment is done in resonance with vibronic states characterized by $k$ values larger than zero.

Based on these results, polyynes display ideal features that allow investigating their vibrational and electronic properties by resonance Raman. First, the Raman modes in the high-frequency region result in an easy detection even at very low sample concentrations. Remarkably, the model and the strategy adopted to justify the intensity pattern exhibited by the overtones in the resonance Raman of sp-carbon chains are valid for polyynes of any length. For longer chains, one expects that the $\alpha$ mode becomes negligible already for C6, and we can expect to observe similar qualitative behavior as that discussed here for C8, C10, and C12, with a possible modulation of the $\beta$ parameter because of the interaction effects with the environment. For instance, such effects have been highlighted by comparing the Raman spectra of hydrogen-capped polyynes in solution with those of the same polyynes encapsulated in carbon nanotubes which shows a remarkable decrease of the position of the $\alpha$ mode by a few tens of wavenumbers. Similar experiments have been performed on long linear carbon chains or confined carbyne in carbon nanotubes showing the effects of the confinement on the Raman bands of sp-carbon chains.

In summary, by exploiting the fine wavelength tunability of the synchrotron radiation, we accomplished the first experimental detection of high-order (up to the IV/V) overtones of the $\alpha$ mode of polyynes, including the combination bands with another collective CC stretching mode ($\beta$ mode). Based on our results, the detailed absorption profile induced by the presence of end groups with $\pi$ electrons (e.g., phenyl groups), often showing conjugation with the $\pi$ orbitals of the sp chain. Third, the huge resonance Raman cross section of polyynes allows easy detection even at very low sample concentrations. Remarkably, the model and the strategy adopted to justify the intensity pattern exhibited by the overtones in the resonance Raman of sp-carbon chains are valid for polyynes of any length. For longer chains, one expects that the $\alpha$ mode becomes negligible already for C6, and we can expect to observe similar qualitative behavior as that discussed here for C8, C10, and C12, with a possible modulation of the $\beta$ parameter because of the interaction effects with the environment. For instance, such effects have been highlighted by comparing the Raman spectra of hydrogen-capped polyynes in solution with those of the same polyynes encapsulated in carbon nanotubes which shows a remarkable decrease of the position of the $\alpha$ mode by a few tens of wavenumbers. Similar experiments have been performed on long linear carbon chains or confined carbyne in carbon nanotubes showing the effects of the confinement on the Raman bands of sp-carbon chains.
electronic and vibrational structure of the ground and first excited state in polyynes can be derived with a one-mode approximation dominated by the $\alpha$ mode. The values of the Huang–Rhys factors determined in such linear carbon structures characterized by triconjugated electrons confined at the nano and molecular scale show a strong and size-dependent electron-phonon coupling, which is appealing for potential exploitation in optoelectronic applications.

We modeled the resonance effect in the framework of Albrecht’s theory of resonance Raman which allowed us to justify the relative intensities of the Raman transitions detected at high vibrational quanta. Polyynes prove to be an ideal system for multi-wavelength resonance Raman spectroscopy, which allows the precise investigation of high-order vibrational transitions due to their well-resolved vibronic features and high-frequency Raman modes.

Methods

Synthesis and separation of hydrogen-capped polyynes

Solutions of size-selected ($n=8,10,12$) hydrogen-capped polyynes (HC$_n$H, from now on C$_n$) were synthesized by pulsed laser ablation in acetonitrile, detected, and separated by high-performance liquid chromatography employing the experimental method described in ref. 55. Their UV-Vis spectra and concentrations are reported in Supplementary Fig. 1a and Supplementary Table 1, respectively.

UV resonance Raman spectroscopy measurements

UV resonance Raman (UVRR) spectra were collected by exploiting the synchrotron-based Raman set-up available at the BL10.2-IUVS beamline of Elettra Sincrotrone Trieste (Italy)\(^\text{1}\). All the samples were measured at a fixed temperature of 288 K using different excitation wavelengths in the deep UV range (see Supplementary Table 1), provided by the emission of synchrotron radiation (SR) source. The exciting wavelengths were set by regulating the undulator gap aperture and using a Czerny-Turner monochromator (Acton SP2750, focal length 750 mm, Princeton Instruments, Acton, MA, USA) equipped with holographic gratings with 3600 groves/mm for monochromating the incoming SR. Raman signal was collected in backscattered geometry, by a single pass of a Czerny-Turner spectrometer (Trivista 557, Princeton Instruments, 750 mm of focal length) equipped with a holographic grating at 1800 g/mm and 3600 g/mm. The spectral resolution was set at $\frac{\text{spectral range}}{100}$ cm$^{-1}$/pixel, depending on the excitation wavelength (e.g., 2.9 cm$^{-1}$/pixel at 206 nm and 1.7 cm$^{-1}$/pixel at 261 nm). The calibration of the spectrometer was standardized using cyclohexane (spectroscopic grade, Sigma Aldrich). The final radiation power on the samples was kept between a few up to tens of $\mu$W (see Supplementary Table 1). Any possible photo-damage effect due to prolonged exposure of the sample to UV radiation was avoided by continuously spinning the sample cell during the measurements.

Fit of UV-Vis absorption and UV resonance Raman spectra

The calculation of the Huang–Rhys factors and nondimensional displacement parameters requires a joint analysis of the UV-Vis absorption and UV resonance Raman spectra (see Supplementary Discussion). Concerning UV-Vis absorption spectra of C$_8$, C$_{10}$, and C$_{12}$, we employed a custom code to fit the vibronic progression with Lorentzian line shapes with the same full width at half maximum. The number of curves used for the fit depends on the number of observed vibronic peaks. We thus calculated the values of the Huang–Rhys factor from the best fits, as described in the Discussion section. Similarly, first-order frequency regions of the UV resonance Raman spectra of C$_8$, C$_{10}$, and C$_{12}$ have been fitted with two Lorentzian curves corresponding to the $\alpha$ and $\beta$ modes. Together with the analysis of UV-Vis absorption spectra, these data allowed us to compute the values of the nondimensional displacement parameters $\delta_{\alpha}$ and $\delta_{\beta}$ needed for the calculation of the resonance Raman intensities (see the next paragraph).

Calculation of the resonance Raman intensities

The prediction of resonance Raman intensities, based on Albrecht’s theory of resonance Raman, has been extensively explained in the Supplementary Discussion. Our Matlab code calculates the Franck–Condon integrals needed in Albrecht’s theory, adopting the displaced harmonic oscillator representation of the vibrational levels of the ground and excited electronic states (see Eq. (27) in the Supplementary Discussion). The evaluation of the Franck–Condon integrals requires the knowledge of the displacement parameters that were found with the joint analysis of UV-Vis absorption spectra and UV resonance Raman spectra (see the previous paragraph). Moreover, we neglect the change of curvature between the ground and excited potential energy surfaces of the $\alpha$ mode (see Discussion). The Franck–Condon integrals were computed, we made the ratio of the intensities (see Eq. (26) in the Supplementary Discussion) to produce the values reported in Fig. 5.

Data availability

The UV-Vis absorption and UV resonance Raman spectroscopy data generated in this study have been deposited in the Zenodo database under accession code https://doi.org/10.5281/zenodo.6798673.

Code availability

The codes that support the findings of this study are available from the corresponding author upon request.

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Author contributions
P.M., S.P., A.L.B., V.R., and C.S.C. conceived the experiment. P.M. and S.P. synthesized the H-capped polyyne samples. P.M., B.R., M.T., V.R., and C.S.C. carried out the UV resonance Raman measurements. M.T., C.C., and P.S. performed theoretical analysis. P.M., M.T., and C.C. performed data analysis. P.M. wrote the paper. All authors discussed the results and contributed to writing subsequent manuscript drafts.

Competing interests
The authors declare no competing interests.

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