Coherent Electron-Lattice Vibrations in *Trans*-Nanopolyacetylene Probed by Raman Scattering

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Unexpectedly high Raman scattering activity of carbon-carbon bond length vibrations was found in polyacetylene nanoparticles. For exciting photon energy in the transparency range of nanopolyacetylene we observed extremely high Raman scattering cross section and high intensity ratio of anti-Stokes to Stokes bands. Furthermore, the Raman activity in *trans*-nanopolyacetylene is characterized by intensive overtones and combinations. We present a qualitative nonlinear model of coherent weakly damped electron-lattice vibrations in ordered *trans*-polyacetylene chains.

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The nature of the ground and lowest excited states in the *trans*-isomer of polyacetylene (PA) has been studied actively for the last two decades. PA is the chemically simplest π-conjugated polymer (Fig. 1, inset) characterized by a strong electron-phonon (e-ph) coupling due to delocalized π electrons. The density of mobile π electrons between adjacent carbon sites in the *trans*-PA chain strongly modulates the strength of their covalent bonding giving a high e-ph coupling and an effective nonlinearity for the lattice motion. Raman scattering (RS) spectroscopy studies of PAs indicate two strong bands associated mainly with carbon-carbon (CC) stretching vibrations C═C and C—C.

In this Letter, we report on an extraordinary behavior of Raman spectra of CC modes in nanopolyacetylene (NPA) from the viewpoint of generally accepted theory of spontaneous Raman scattering based, for example, on the Albrecht approach [1]. The observed Raman activity in *trans*-NPA can be described as "transparency range resonant RS" (RRS) and, to the best of our knowledge, has not been observed in any material. We associate high Raman activity in PA with collective CC vibrations interacting via π-conjugated electrons. We succeeded in observing this Raman activity owing to the highly ordered structure of NPA that differentiates it from other known types of PA. It is well known that disorder is a crucial factor affecting the properties of π-conjugated chains. At the same time, we have managed to prepare a low-defect type of PA in the form of nanoparticles [2] in which PA chains form an ordered molecular structure. The main observed features of RS in *trans*-NPA are as follows: for exciting photon energy far below the main absorption band, an unexpectedly high (i) Raman cross section and (ii) ratio of anti-Stokes (AS) to Stokes intensities, as well as (iii) a long and intensive progression of overtones and combinations. These features usually indicate the case of RRS thoroughly studied in connection with the effect of phonon frequency dispersion with exciting photon energy [3,4]. Much less attention was given to Raman intensity studies in π-conjugated systems. Only in recent works [5,6] a superlinear increase of Raman intensity with the conjugation length was studied on isolated chains in detail. As was recently shown for various π-conjugated polymers [7], the RRS dispersion of the CC modes is closely related to low-lying optically forbidden A_g states. The intensive vibrational structure of the preresonance Raman excitation spectrum in *trans*-β-carotene was also assigned to a subgap A_g state [8]. Following the generally accepted Raman theory, we argue below that the intragap A_g states in NPA hardly could be active in RS but silent in optical absorption. To interpret our observations, we formulate a qualitative model of coherent electron-lattice vibrations in *trans*-PA referred to as the nonlinear model. This model seems closely related to actively studied breather excitations [9] which are e-ph coupled nonlinear excitations involving persistent intrinsically localized phonon modes. The latter were observed in recent RRS studies on Pt-Cl chains [10]. Our nonlinear model gives us a framework in which the experimental results are presented. The key feature of this model is a coherent

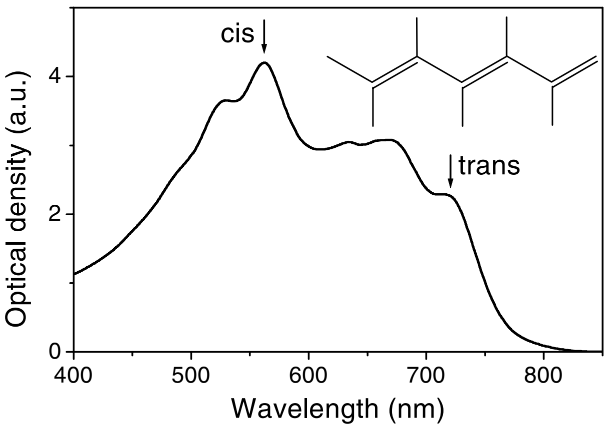

FIG. 1. Absorption spectrum of a NPA film at room temperature. Arrows indicate the zero-phonon lines of both isomers. Inset shows the geometry of a *trans*-PA chain fragment.

mode which is a collective mode of nonlinear coupled partial CC vibrations. We suggest that this mode involves a large number of CC vibrations in the PA nanoparticle. In the in-phase region of this coherent mode [11], either the C═C or the C—C bonds vibrate in-phase but the adjacent bonds (C═C and C—C) vibrate out-of-phase that corresponds to a $k = 0$ optical phonon (Fig. 1, inset). For this synchronous motion the Raman intensity is strongly enhanced because it is proportional to the squared sum of scattering amplitudes of the partial CC vibrations. The effect of synchronization is due to e-ph coupling and is an analog of frequency lock-in in nonlinear coupled oscillators. The characteristic synchronization length L can be roughly estimated as the propagation length of an electron with Fermi velocity V_F during the C═C vibration period ν_3^{-1}. For $V_F \simeq 1 \times 10^8$ cm/s [12] $L \sim V_F/\nu_3$ corresponds to an ~200 CC bonds chain that is on the order of the typical size of our PA nanoparticle. The in-phase mode corresponds to a vibration along the so-called effective conjugation coordinate (ECC) [4], which is an extremely fruitful notion for analyzing vibrational properties of many π-conjugated systems [4–6]. Note that enhanced CC vibrational activity assigned to a collective ECC-like mode is observed in IR spectra of aromatic π-conjugated hydrocarbons [13]. On the other hand, it was stressed earlier [14] that the ECC is a heuristically constructed internal coordinate and that the ECC mode is in general not a normal mode. We postulate that the coherent mode is an intrinsic mode of the ordered *trans*-PA chains where coherence appears as a result of *nonlinear* coupling.

The geometry of an ideal infinite *trans*-PA chain is a series of almost equidistant situated carbon sites with an in-plane zigzag of CC bonds (Fig. 1, inset). The difference in C—C and C═C bond lengths, that is the alternation parameter, is ≃0.08 Å. This ideal chain model is supported by *ab initio* calculations for short polyene chains [15]. There are two main factors responsible for the distinction between real and ideal π-conjugated chains. The first is a chain end effect: the almost isolated C═C bonds at the ends of the chain impose a bond length alternation on neighboring CC bonds. At the same time, as follows from various simulations, the chain end effect decreases strongly within a few CC bonds [15]. The second factor is a local field effect as the real PA chains are surrounded by others. Recent calculations [16] show that the local field effect is very strong in the *trans*-PA crystal structure changing by an order of magnitude the nonlinear polarizability. Therefore, interchain disorder can produce a fluctuating local field, which is different in each chain cell, thereby suppressing the translation order. These effects seem to be very essential in real PA samples characterized by a broad distribution of conjugation lengths. It is reasonable to suppose that for real PA samples the coherent mode is possible in the middle of rather long conjugated chains with low translational disorder as well as across the chains. Obviously, the closer the partial frequencies of neighboring CC cells, the more probable synchronization of the coupled oscillators. Structural and thermal disorder leads to misphasing the coherent vibrations. A structural defect in the chain, for example, an sp^3-hybridized carbon site, breaks π-conjugation suppressing delocalization of π electrons and therefore coupling of the CC partial oscillators. Thus, according to our nonlinear model, the coherent mode can appear in real *trans*-PA chains with low structural and thermal disorder.

NPA is a highly ordered form of PA in which PA nanoparticles are dispersed in a polyvinylbutyral matrix [2]. Each nanoparticle looks like a small molecular crystal. The PA content in polyvinylbutyral was ≃1%. Films of thickness 2–100 μm with optical densities ≳0.5 were used. Liquid samples were strongly diluted butanol-polyvinylbutyral-PA-nanoparticles compositions. *Cis/trans* ratio in NPA was evaluated from the absorption spectrum (Fig. 1) as 50%/50%. Conjugated chains in NPA have lengths ≲30 nm with neat optical gap at 750 nm (Fig. 1) and are characterized by a narrow length distribution. For example, if other types of PAs demonstrate RRS dispersion of the C═C band ~150 cm^{-1} [3], the dispersion in NPA is ~15 cm^{-1} [17]. Raman spectra of NPA were measured at room temperature with Fourier transform infrared (FTIR) and grating spectrometers using the backscattering geometry for a number of excitation wavelengths in the range 1064–488 nm [17]. We discuss here only three experimental observations indicated in the introduction for *trans*-NPA Raman bands ν_1 and ν_3 associated mainly with stretching C—C and C═C vibrations, respectively.

(i) We observed that the Raman cross section of *trans*-NPA unexpectedly high for excitation in its transparency range. The integral Raman intensity was proportional to the excitation intensity [17] that excludes any optically stimulated process. Figure 2 shows the FTIR Raman spectrum of a liquid sample for excitation at 1064 nm. From Fig. 2 we evaluated the cross section of *trans*-NPA

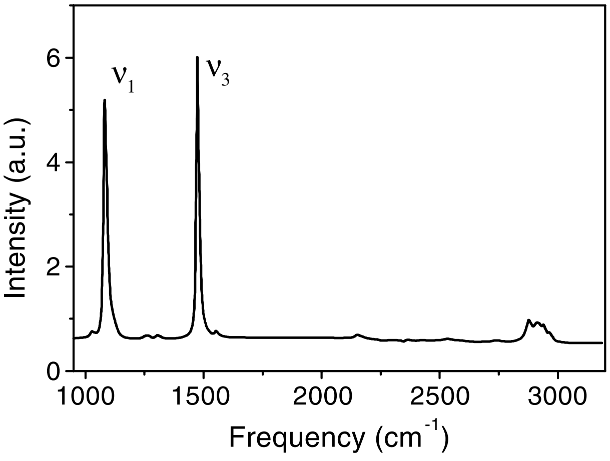

FIG. 2. Raman spectrum of a NPA liquid sample recorded at 1064 nm.

with respect to the most intense band of the solvent at $\sim 2900\ \mathrm{cm}^{-1}$. Taking into account the volume concentration of NPA 2×10^{-4} and the ω^4 correction factor, we obtain that the integral *trans*-NPA Raman cross section for both ν_1 and ν_3 bands per unit volume is higher than that of the solvent by a factor of $\sim 2 \times 10^4$. Taking the absolute cross section for alcohol from Ref. [18] measured at 488 nm with the ω^4 factor, we evaluated the absolute integral cross section of the isotropic *trans*-NPA for ν_3 mode per carbon in steradian $\sim 5 \times 10^{-28}\ \mathrm{cm}^2/\mathrm{sr}$ for excitation at 1064 nm. This value is only one order less than the RRS cross section of Shirakawa's *trans*-PA measured in Ref. [19] (taken with corresponding correction factors). The *trans*-NPA Raman cross section is so high that one can suppose the case of RRS. At the same time, NPA is transparent below its absorption edge. The absorption coefficient in the transparency range is at least 4 orders less than that for the main dipole-allowed transition (Fig. 1). This estimate is also obtained from our recent photothermal spectroscopy studies on NPA films [20] in which low absorption in the near-IR is readily detected.

(ii) Figure 3 shows the FTIR Raman spectrum of a NPA film for both Stokes and AS bands recorded at 1064 nm. The AS bands are a mirror image of the Stokes bands within our experimental error. The AS intensities are unexpectedly high with respect to the Stokes ones since the room-temperature Boltzmann factors for the ν_1 and ν_3 modes are $\sim 5 \times 10^{-3}$ and $\sim 6 \times 10^{-4}$, respectively. We stress that all the photon energies (pump, Stokes, and AS) are far below (>0.4 eV) the NPA absorption edge (Fig. 1). Consequently, preresonance effects associated with the electronic absorption band can be neglected. Assuming nonresonant RS and taking into account the ω^4 correction factor, we obtain from Fig. 3 that the integral AS intensities for both ν_1 and ν_3 bands correspond to an effective vibrational temperature $\simeq 700$ K. This temperature is considerably higher than the temperature of thermal destruction of both PA and polyvinylbutyral matrix. We estimate the heating of the sample <70 K from the temperature dependence of the ν_1 and ν_3 frequencies [21].

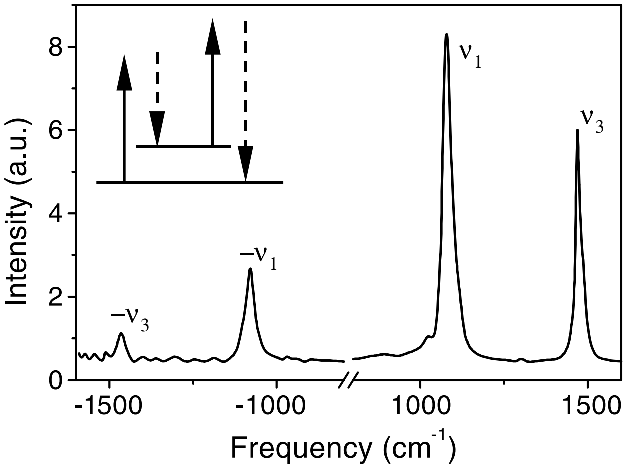

FIG. 3. Raman spectrum of a NPA film recorded at 1064 nm for excitation intensity $<20\ \mathrm{kW/cm}^2$. Inset illustrates a process in which pump (solid arrow) and scattered (dashed arrow) photons excite the coherent mode giving a high AS signal obtained with the second photon pair.

It is reasonable to relate the high AS/Stokes ratio to the non-Boltzmann population of the ν_1 and ν_3 modes. We suppose that the AS scattering may occur by a process depicted in Fig. 3, inset. This mechanism of AS scattering implies a very long lifetime of the coherent mode excited by the first photon pair. Note that an unexpectedly long decay time of the transient photoinduced AS signal from the ν_1 mode of *trans*-PA was reported [22] indicating a long nonequilibrium phonon relaxation process.

(iii) At all excitation wavelengths the Raman spectra of *trans*-NPA demonstrate intensive overtones and combinations of the ν_1 and ν_3 modes. Up to ten bands with frequencies $\simeq n\nu_1 + m\nu_3$ $(m, n = 1, 2, \ldots)$ are observed [17]. When the excitation wavelength is within the NPA absorption band, the intensities of some $n\nu_1 + m\nu_3$ bands exceed the ν_1 and ν_3 fundamentals [17]. Figure 4 shows the NPA Raman spectrum for excitation at 785 nm for which all the CC Raman bands are in the transparency range. From Fig. 4 after the ω^4 correction, we obtain that the integral oscillator strength of the $\sim n\nu_1 + m\nu_3$ bands is $\simeq 30\%$ of that for both ν_1 and ν_3 fundamentals. Consequently, nonlinearity of the CC vibrations is high and hardly can be properly considered as a small perturbation. Analogously, the oscillator strength for the first CC combination $(\nu_1 + \nu_3)$ is $\simeq 20\%$ of the half-sum of that for the ν_1 and ν_3 fundamentals. These observations are beyond the standard normal mode analysis based on independent harmonic vibrations ν_1 and ν_3 and indicate that anharmonicity giving their coupling is very essential in *trans*-PA. Thus, the intensive $n\nu_1 + m\nu_3$ bands support our suggestion that the coherent mode is an eigenmode of a strongly nonlinear system consisting of π-conjugated electrons and CH units.

Suppose that an intragap A_g state of *trans*-NPA participates in RS. Then, in the context of Albrecht's theory

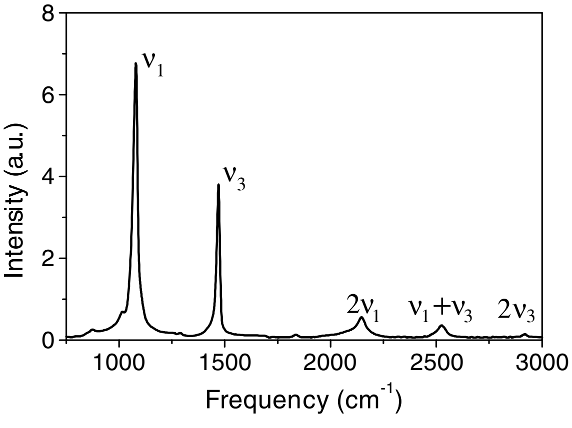

FIG. 4. Raman spectrum of a NPA film recorded at 785 nm.

[1], we should invoke a mechanism of oscillator strength transfer from the main dipole-allowed state $1B_u$. This Herzberg-Teller coupling was used for the interpretation of the preresonant Raman spectrum in various molecules, for example, in *trans*-β-carotene [8]. It implies that a forbidden state closely spaced to the dipole-allowed one becomes visible both in Raman and absorption spectra. This mechanism is hardly essential for our observations in *trans*-NPA indicating that we should have a deep intragap state which is Raman active but is silent in optical absorption. Note that interference effects may enhance the contribution of a forbidden state in Raman polarizability compared to that in linear absorption. However, they are visible as a feature on the tail of the dipole-allowed band [23].

Strong interchain interactions in PA [16] suggest that the coherent mode may extend over large distances across the conjugated chains as well. We conjecture that the coherent mode is a type of macrovibration characterized by long lifetimes that is consistent with the observed high AS signal. Note that the lifetime of coherent vibrations in π-conjugated systems measured in time-resolved experiments can be long. For instance, weakly damping CC stretching vibrations excited by a few fs optical pulses were observed in a finite analog of the *trans*-PA chain, *trans*-β-carotene [24], and in polydiacetylene [25]. Furthermore, photoinduced states in π-conjugated chains, including *trans*-NPA [26], are characterized by a number of relaxation times extending from the femtosecond to the millisecond time scales. It is quite possible that the coherent mode is a type of breather [9].

In conclusion, we observed an unexpectedly high Raman activity of CC stretching vibrations in an ordered form of PA, NPA. According to our nonlinear model, the partial CC vibrations form a coherent mode in ordered *trans*-PA chains due to extended π-conjugation giving strong e-ph coupling. The coherent mode is an intrinsic mode of a strongly nonlinear electron-lattice system of *trans*-PA. The observed long progression of overtones and combinations is a signature of this nonlinearity. The coherent mode includes many partial CC vibrations and like a macrovibration is characterized by a long lifetime that we deduce from the high AS/Stokes ratio. In the in-phase region of the coherent mode, the CC vibrations are synchronized over long distances leading to high Raman intensity.

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