TEMPERATURE EVOLUTION OF ELECTRONIC AND LATTICE CONFIGURATIONS IN HIGHLY ORDERED TRANS-POLYACETYLENE

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We have studied temperature evolution of optical absorption and Raman scattering spectra of trans-cis blend of 'soluble' polyacetylene in polyvinylbutyral/butanol mixture. With temperature decrease the reversible reconstruction of electronic and lattice system of trans-$(CH)_x$ occurs: the electronic energy gap contracts with high mobility of 0.4 meV/K and the vibrational modes are modified. The experimental data obtained are interpreted in terms of peculiar interaction of π-conjugated electrons with lattice fluctuations.

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During the last 15 years polyacetylene, $(CH)_x$, attracts special attention as a unique research object. Firstly, $(CH)_x$ is chemically the simplest conjugated polymer with conjugated bonds of π electrons and, therefore, it could serve as a model for other conjugated polymers. Also, in terms of solid state physics $(CH)_x$ is the simplest example of a quasi one-dimensional (1D) semiconductor. Another important feature of $(CH)_x$ is strong electron-phonon coupling, allowing the initial electronic excitation to relax into a polaron-like quasi-particle, e.g., a soliton for the trans-$(CH)_x$ case [1]. The solitons are thought to be responsible for many optical and transport properties of trans-$(CH)_x$.

Despite the considerable efforts, however, several key issues concerning trans-$(CH)_x$, such as the origin of the optical absorption edge, configurations of the ground and the lowest excited states, etc., remain unclear till now. The main reason of such situation is that in real-life samples disorder has always obscured the true picture of excitations intrinsic for the polymer chain. And, inevitably, investigators have encountered the problem of distinguishing the intrinsic properties of trans-$(CH)_x$ from the extrinsic, disorder-induced properties. While perfectly ordered or macroscopic single-crystalline samples of $(CH)_x$ are still unavailable, we have tried to obviate disorder related problems by using a 'soluble' form of $(CH)_x$. In this case, $(CH)_x$ is represented by small particles composed of ordered chains, the former being dispersed within a 'solvent' matrix. Our earlier experiments with films of this 'soluble' $(CH)_x$ have demonstrated that the small particles of $(CH)_x$ exhibit properties characteristic for crystalline $(CH)_x$ [2] and, importantly, this $(CH)_x$ particles are free of disorder.

In the present paper we report the first observations of high mobility of the ground state configuration of trans-$(CH)_x$ under effect of temperature. Using the 'solutions' of $(CH)_x$, we have demonstrated that the strength of interaction of π

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electrons with lattice in trans-$(CH)_x$ is readily changed by temperature, leading to qualitative changes in the electron-lattice configuration revealed in both Raman and optical absorption spectra.

The samples were prepared by the method described in Ref.[3]. Polymer chains in the 'soluble' $(CH)_x$ are organized in an ordered crystal structure (looking like matches in a matchbox) with typical size of ~ 10 nm. Such small particles of $(CH)_x$ are 'dissolved' in polyvinylbutyral-butanol (PVB-Bu) matrix composition. The total content of $(CH)_x$ in PVB was $\sim 2\%$, while the concentration of PVB in butanol was $< 1\%$ by weight. From the absorption spectrum of the cis-trans blend we estimated that there were $\simeq 65\%$ trans and $\simeq 35\%$ cis-particles. Cryogenically cooled samples with optical densities ~ 1 and ~ 10 (for optical absorption and Raman scattering measurements, respectively) were used in this work. By using the samples in glass cells, optical absorption measurements were performed at 300–190 K, while Raman spectra were run at 300–210 K. The lowest temperature was chosen to be slightly higher than the freezing point of the solvent, 183 K. Absorption spectra were measured by using a Cary 219 spectrophotometer. Raman spectra were recorded with the aid of a Perkin-Elmer NIR-FT Raman attachment coupled with a FTIR spectrometer. The excitation photon energy (1.17 eV) was in the transparency range of cis and trans-$(CH)_x$.

By changing the sample temperature, an evolution of the absorption spectrum of 'soluble' $(CH)_x$ was monitored. The absorption spectra for both cis and trans-isomers revealed a vibronic structure at all temperatures studied. However, the temperature behavior of trans and cis-$(CH)_x$ spectra differs dramatically. Fig.1 shows that, for trans-$(CH)_x$, with temperature change three effects can be observed: thermochromism, change of the vibronic structure and broadening of the latter. A prominent peculiarity of the trans-$(CH)_x$ absorption spectrum is the large red shift of the whole spectrum with temperature decrease (Fig. 1), the low energy feature at 1.71 eV (190 K) shifts with a thermochromic coefficient of $\simeq 0.4$ meV/K. The lowest energy spectral features characteristic for 'soluble' trans and cis-$(CH)_x$ correspond to zero-phonon transitions or energy gaps E_g peaked at 1.71 and 2.19 eV (190 K), respectively. We note that the measured energy gaps values for the 'soluble' $(CH)_x$ coincide with those reported for other types of $(CH)_x$ [1].
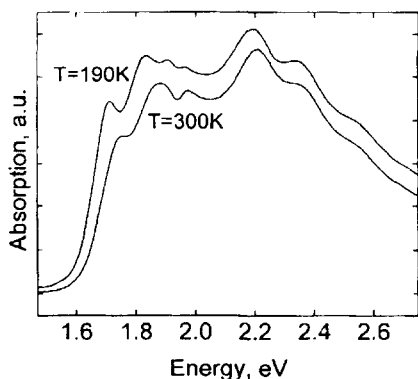

Fig.1 Absorption spectra of a 'solution' of trans-cis-$(CH)_x$ blend at room and low temperatures

Although the cis-isomer also shows thermochromism and vibronic sidebands broadening, the thermochromicity in this case is considerably weaker than for the

trans-isomer (Fig. 1). The maximum of the cis-$(CH)_x$ absorption spectrum shifts with the thermochromic coefficient of $\simeq 0.15$ meV/K. Splitting of the cis-$(CH)_x$ vibronic sidebands does not change with temperature increase, they only become somewhat broader.

Another prominent feature of the temperature evolution of the trans-$(CH)_x$ spectrum is the change of its vibronic structure. The vibronic sidebands are split from the zero-phonon line and are found in the range of 1000–2000 cm^{-1}. At low temperatures the three vibronic sidebands are clearly seen (Fig. 1) in addition to the zero-phonon line E_g, while at room temperature we have observed only two vibronic sidebands. Fig. 1 shows unambiguously, however, that the splitting between the second and first vibronic sidebands markedly varies with temperature. The observed change of the vibronic structure can not be explained by thermal broadening effect, rather it indicates the different configurations of ground and excited states for the trans-$(CH)_x$ at room temperature. Although vibronic frequencies can shift due to trivial thermal expansion effect, the observed shifts of the vibronic frequencies are too large to be justified within the Grüneisen approximation. We show below that the observed temperature-induced reconstruction of the trans-$(CH)_x$ spectrum is connected with changes of π electron conjugation in the polymer chain.
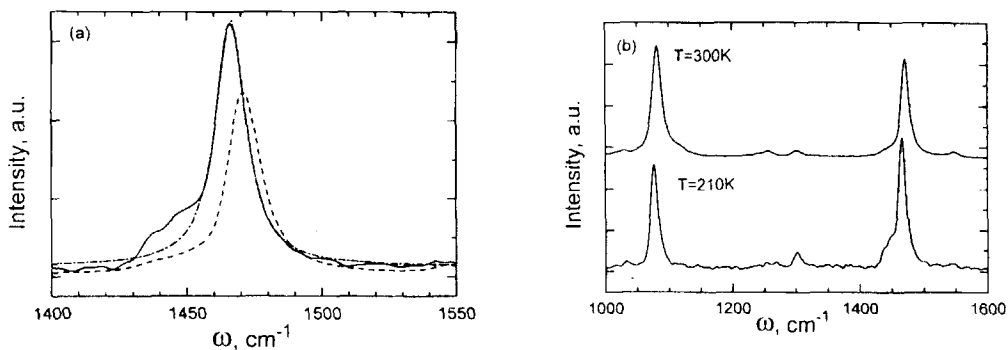

Fig.2 (a) Raman scattering spectra of a 'solution' of trans-cis-$(CH)_x$ blend at room and low temperatures. (b) The (C=C) stretching mode line ω_3 at room (dashed) and low (solid) temperatures. The low temperature spectrum is fitted by Lorentzian curve (dash-dotted)

With Raman scattering experiments we demonstrate that vibrational frequencies of trans-$(CH)_x$ are also highly sensitive to temperature. Fig. 2 shows typical NIR-FT Raman spectra of $(CH)_x$ obtainable at low (210 K) and room temperatures. Notably, the complete set of Raman lines known from literature for cis and trans-$(CH)_x$ [4–6] has been observed in the range of 1000–2000 cm^{-1}. Specifically, the three Raman lines for trans-$(CH)_x$ at $\omega_1 = 1081$, $\omega_2 = 1300$, and $\omega_3 = 1471$ cm^{-1} and the two lines for cis-$(CH)_x$ (1255 and 1547 cm^{-1}) were observed at room temperature. It is known from studies on polyenes [6] that ω_1 and ω_3 Raman lines can be assigned to single (C–C) and double (C=C) bond stretching modes, respectively. Our analysis has shown that ω_1 and ω_3 Raman lines are good Lorentzians with ~ 15 cm^{-1} (210 K) width (Fig. 2). At room temperature the linewidths were $\lesssim 30\%$ broader than at 210 K.

Moreover, in analogy to the absorption spectra, the Raman features of trans and cis-$(CH)_x$ exhibited markedly different behavior. Firstly, the Raman spectrum of trans-$(CH)_x$ has dramatically changed with temperature. Secondly, despite the trans/cis ratio for the samples studied was $\simeq 2$, the intensities of the Raman lines belonging to cis-$(CH)_x$ were ~ 30 times weaker compared to intensities of lines at ω_1 and ω_3 characteristic for trans-$(CH)_x$. Although the concentrations of $(CH)_x$ in solution studied were $< 0.02\%$, the Raman spectra gave no confidently detectable lines assignable to the solvent matrix (PVB-Bu). This clearly shows the enhanced Raman response of the conjugated polymer ($(CH)_x$) with respect to the host non-conjugated polymer (PVB).

Upon temperature decrease, we observed the $\simeq 5$ cm^{-1} (0.05 cm^{-1}/K) red shifts of the Raman lines belonging to (C=C) and (C-C) stretching modes for the trans-$(CH)_x$ (Fig.2a). This effect was reported for other types of trans-$(CH)_x$ [7, 8] and it is not related to thermal expansion which should give the opposite sign. Such behavior of vibrational frequencies in conjugated polymers with temperature decrease can be explained by an increase of the 'effective conjugation length' [6, 9]. It is known that conjugated π electrons tend to attenuate the double (C=C) bond strength with increasing the chain length, thus softening the vibrational modes. The π-conjugated system, however, is thought to be a highly sensitive superstructure which can be easily disturbed by structural defects. Thus, for example, thermal fluctuations leading to the out of chain plane vibrations can break the conjugation, making a conjugation defect [9]. As a result, the averaged conjugation length decreases and the phonons coupled with π electrons become harder.

More strictly, the conjugated π electrons renormalize the bare optical phonons frequencies ω_i^0. According to the 1D model of $(CH)_x$ chain, there exists the single Raman active mode [10] which appears with renormalization by π electrons of the zone-center bare optical phonon ω_0: $\omega = \omega^0(2\lambda)^{1/2}$. Here λ is the renormalization parameter which characterizes the strength of electron-phonon coupling and it drives the phonon frequency. Temperature decreasing improves the structural order that enhances conjugation (λ decreases or the effective conjugation length increases) and phonons become softer [11]. The more realistic model describes the planar 'zig-zag' $(CH)_x$ chain [12]. In terms of this model, which includes three Raman-active modes, Vardeny et.al. have explained a number of features of $(CH)_x$ observed in resonant Raman scattering [11, 13]. Their analysis showed that the ω_3 Raman band belongs to almost pure (C=C) stretching mode and this mode is the most strongly coupled with π electrons. The latter conclusion agrees with the results of our work in that the dominant temperature-induced changes have been observed for the ω_3 line.

Indeed, the most striking result of our Raman scattering experiments is the temperature-induced change of the lineshape of the (C=C) stretching mode. Fig.2b shows that upon temperature decrease the ω_3 lineshape changes dramatically leading to appearance of a low-frequency shoulder. At 210 K the shoulder has ~ 20 cm^{-1} width and extends down to 1435 cm^{-1}. According to the interpretation by Vardeny et.al. [11], there exists a distribution of electron-phonon coupling parameter λ for a trans-$(CH)_x$ sample or, in other words, a distribution of lengths of conjugated chains. This distribution can be induced by disorder, but in our case it is the intrinsic property of trans-$(CH)_x$ chain. With temperature decrease the conjugation

degree increases modifying the lattice configuration, and new vibrations coupled with π electrons appear.

Thus, the observed temperature evolution of both the Raman scattering and optical absorption spectra clearly correlate in that they reflect the same effect: the reversible reconstruction of the ground state configuration of trans-$(CH)_x$ chain with temperature. Such correlation can be explained if we suppose that the strength of electron-phonon coupling in trans-$(CH)_x$ is the most sensitive parameter, which can be readily changed by temperature. The energy gap of the Peierls chain depends on the electron-phonon parameter λ as $E_g \sim \exp(-1/2\lambda)$ [11, 12]. At the same time, the Raman frequencies are related to λ by the 'product rule' [11, 12] $2\lambda \sim (\omega_1\omega_2\omega_3)^2$. Thus, the temperature drop increases the strength of electron-phonon coupling that leads to red shifts observed in both the Raman and absorption spectra of trans-$(CH)_x$. For small temperature-induced changes in the energy gap and the Raman frequencies we have $\delta E_g/E_g = 1/2\lambda\,\delta\lambda/\lambda$ and $\delta\lambda/2\lambda \simeq \delta\omega_1/\omega_1 + \delta\omega_3/\omega_3$. From our data we obtain $\lambda \simeq 0.35$ at 210 K and it is 1.5% larger at room temperature.

However, in the case of cis-$(CH)_x$ the lattice geometry is not suitable for extended conjugation of π electrons. This leads to a stable dimerized structure which is considerably less sensitive to temperature than the trans-$(CH)_x$. This consequence is supported by the observed weak temperature sensitivity of the cis-$(CH)_x$ absorption spectrum and by the indifference of its vibronic structure to temperature. The large difference in strength of interaction of π electrons with lattice, existing for trans and cis-isomers of $(CH)_x$, is also supported by the observed high ratio of their relative Raman activities. It should be noted here that the exciting optical frequency used in this work (1.17 eV) was far from resonant conditions for both trans and cis-isomers (1.7 and 2.2 eV, respectively).

In conclusion, for highly ordered 'soluble' form of $(CH)_x$, we have found that the temperature evolution of its Raman scattering and optical absorption specrta reflects essentially the same effect: the reversible reconstruction of the ground state configuration of the trans-$(CH)_x$ chain with temperature. By cooling, the new frequencies in the Raman scattering spectrum appear, the electronic energy gap contracts, and the vibronic structure of optical absorption spectrum is modified.

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